



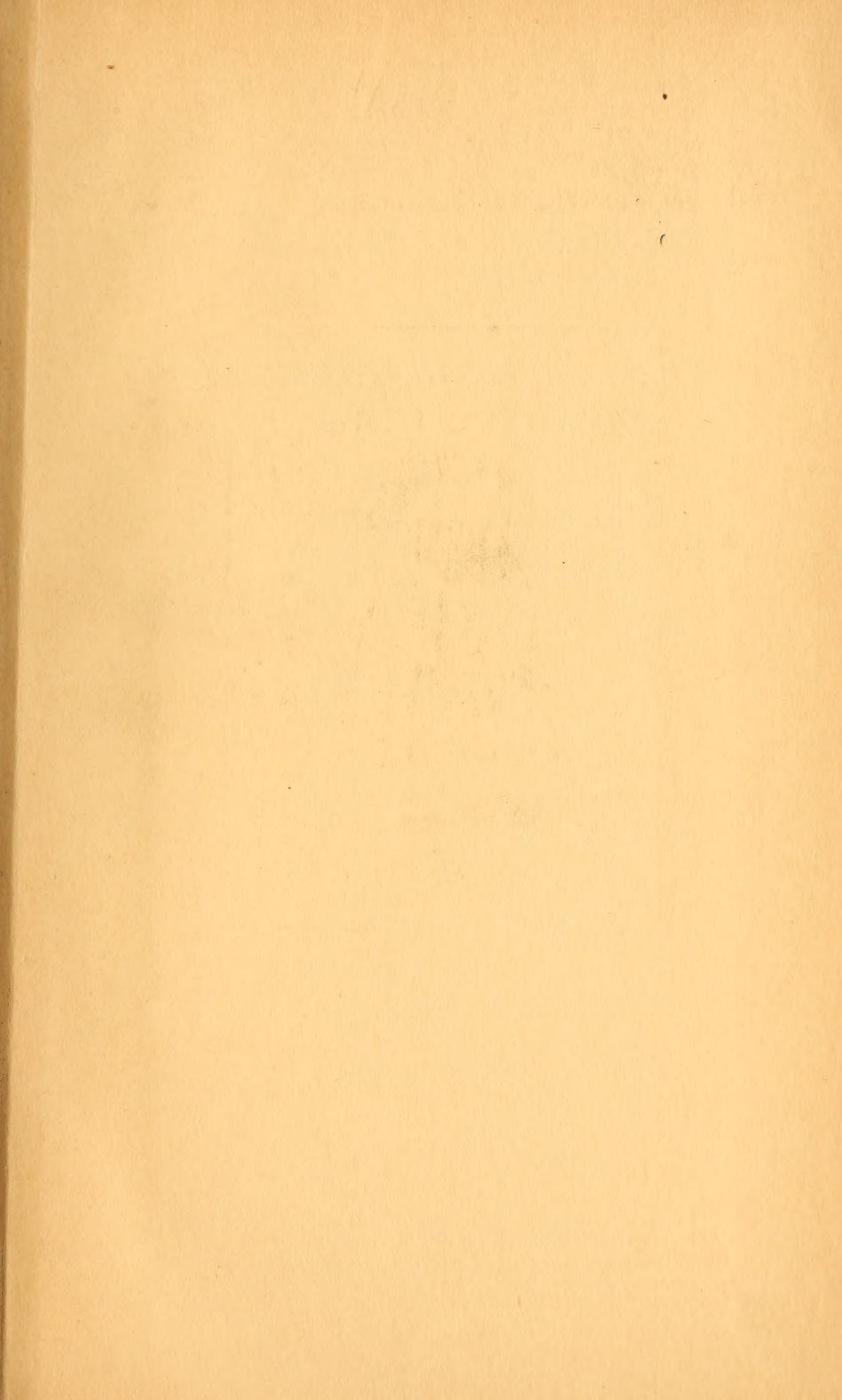
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CONDUCTED BY

SIR OLIVER JOSEPH LODGE, D.Sc., LL.D., F.R.S.  
SIR JOSEPH JOHN THOMSON, M.A., Sc.D., LL.D., F.R.S.  
JOHN JOLY, M.A., D.Sc., F.R.S., F.G.S.  
GEORGE CAREY FOSTER, B.A., LL.D., F.R.S.

AND

WILLIAM FRANCIS, F.L.S.

---

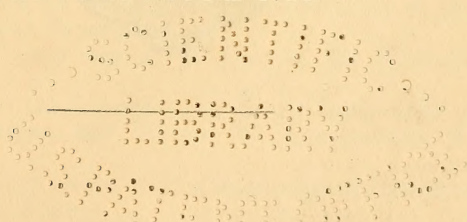
"Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster  
vilior quia ex alienis libamus ut apes." JUST. *Inst. Polit.* lib. i. cap. i. Not.

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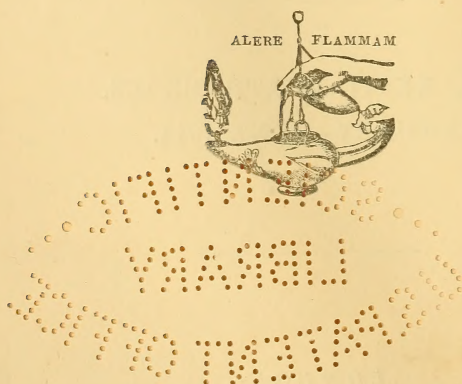
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“Meditationis est perscrutari occulta; contemplationis est admirari  
perspicua . . . . Admiratio generat quaestionem, quaestio investigationem,  
investigatio inventionem.”—*Hugo de S. Victore.*

—“Cur spirent venti, cur terra dehiscat,  
Cur mare turgescat, pelago cur tantus amaror,  
Cur caput obscura Phœbus ferrugine condant,  
Quid toties diros cogat flagrare cometas,  
Quid pariat nubes, veniant cur fulmina coelo,  
Quo micet igne Iris, superos quis conciat orbes  
Tam vario motu.”

*J. B. Pinelli ad Mazonium.*





# CONTENTS OF VOL. XXVII.

(SIXTH SERIES).

NUMBER CLVII.—JANUARY 1914.

	Page
Prof. J. Joly on the Temperature of Sublimation .....	1
Prof. J. H. Jeans on the Interaction between Radiation and Free Electrons .....	14
Prof. A. Gray on Canonical Relations in General Dynamics .	22
Mr. H. R. Hassé on the Equations of Electrodynamics for Moving Ponderable Media and the Principle of Relativity .	43
Mr. H. H. Poole on the Thermal Conductivity and Specific Heat of Granite and Basalt at High Temperatures .....	58
Dr. Norman Campbell on Delta Rays from Gases .....	83
Mr. E. Talbot Paris and Prof. A. W. Porter: An Experiment on Rotatory Polarization in Liquids .....	91
Mr. F. Simeon on the Viscosity of Calcium Chloride Solutions .....	95
Lord Rayleigh: Further Applications of Bessel's Functions of high order to the Whispering Gallery and allied Problems .....	100
Mr. W. N. Fenninger on the Hall Effect in Liquid and Solid Mercury .....	109
Dr. A. S. Russell and Mr. J. Chadwick on the $\gamma$ Rays of Polonium, Radium, and Radioactinium .....	112
Prof. H. Nagaoka and Mr. T. Takamine on Crossed Spectra obtained by Combinations of Different Interferometers, and their Applications to the Measurement of Difference in Wave-lengths. (Plate I.) .....	126
Dr. H. Bateman on the Classification of Electromagnetic Fields .....	136
Mr. R. J. Pocock on the Action of a disturbing Force in the restricted Problem of Three Bodies .....	147
Mr. J. Rose-Innes on the Physical Interpretation of the Michelson-Morley Experiment ..	150
Messrs. R. M. Deeley and P. H. Parr on the Hintereis Glacier .....	153
Mr. H. Moore on the Ionization in various Compounds of Carbon, Hydrogen, and Oxygen by homogeneous X- radiation .....	177
Dr. Irving Langmuir on the Heat of Formation of Hydrogen from Hydrogen Atoms .....	188
Dr. B. Hodgson on Heating Effects at the Anode in Vacuum- Tubes .....	189
Mr. C. H. Lander on the Application of Graphical Methods to the Solution of Problems on Struts and Tie-Rods with Lateral and Non-Axial Loads .....	203

	Page
Prof. G. W. O. Howe on the Effect of Ionization of Air on Electrical Oscillations, and its bearing on Long-Distance Wireless Telegraphy.....	213
Mr. F. Soddy on the Existence of Uranium Y. (Plate II.)..	215
Notices respecting New Books:—	
Researches of the U.S. Department of Terrestrial Magnetism. Land Magnetic Observations 1905-1910	222
Mr. W. Makower and Dr. H. Geiger's Practical Measure- ments in Radio-activity .....	222
Proceedings of the Geological Society .....	223

## NUMBER CLVIII.—FEBRUARY.

Mr. D. C. H. Florance on Secondary $\gamma$ Radiation .....	225
Prof. E. P. Adams on some Electromagnetic Effects related to the Hall Effect .....	244
Mr. H. Richardson: Analysis of the $\gamma$ Rays from the Uranium Products .....	252
Prof. W. Peddie on the Structure of the Atom .....	257
Prof. J. S. Townsend on the Energy required to Ionize a Molecule by Collision .....	269
Mr. C. W. H. Foord on Air-Pressures used in Playing Reed Instruments. (Plate III.) .....	271
Mr. C. D. Child on Ionization in the Unstriated Discharge and in the Arc .....	277
Mr. W. J. Walker on the Relationship between the Viscosity, Density, and Temperature of Salt Solutions. (Plate IV.)..	288
Mr. H. A. McTaggart on the Electrification at Liquid-Gas Surfaces .....	297
Mr. C. G. Darwin on the Theory of X-Ray Reflexion .....	315
Prof. H. Nagaoka and Mr. T. Takamine: Anomalous Zeeman Effect in Satellites of Mercury Lines. (Plate V.) .....	333
Mr. Gervaise Le Bas on the Theory of Molecular Volumes..	344
Dr. J. R. Ashworth on the Anhyseretic Magnetic Properties of Iron and Nickel.—Part I. The Relation of Magnetic Intensity to Field Strength and Temperature .....	357
Mr. G. W. White on the Properties of Selenium Blocks ....	370
Dr. E. H. Barton on Ionization and Wireless Telegraphy ..	381
Dr. H. A. Wilson on the Distribution of Scattered Röntgen Radiation .....	383
Mr. J. R. Wilton on Deep Water Waves .....	385
Prof. A. S. Eve on the Number of Ions produced by the Gamma Radiation from Radium....	394
Notices respecting New Books:—	
Annals of the Astrophysical Observatory of the Smith- sonian Institution, Vol. III. ....	396



## NUMBER CLIX.—MARCH.

	Page
Dr. F. P. Kerschbaum: Interference Experiments in a Highly Rarefied Gas. (Plate VI.) .....	397
Dr. A. M. Tyndall and Mr. H. G. Hughes on Cathode Disintegration in a Vacuum Tube.....	415
Prof. A. Gray: Notes on Electricity and Magnetism.— 1. The "Rails and Slider" Magneto-machine. 2. Permanent Magnets and Dynamical Theory.....	428
Lord Rayleigh: Further Calculations concerning the Momentum of Progressive Waves .....	436
Dr. W. F. G. Swann on the Expression for the Electrical Conductivity of Metals as deduced from the Electron Theory .....	441
Prof. A. van den Broek on Nuclear Electrons .....	455
Mr. C. R. Englund on the Electron Atmosphere (?) of Metals .....	457
Prof. F. P. Worley on the Decline of the Hypothesis of Ionic Dissociation .....	459
Prof. Dr. E. Waetzmann: A Note on Prof. E. H. Barton's Article "Range and Sharpness of Resonance under Sustained Forcing and their Variations with Pitch" .....	467
Mr. G. H. Livens on the Intrinsic Optical Activity of Isotropic Media .....	468
Mr. A. Ll. Hughes on the Long-Wave Limits of the Normal Photoelectric Effect .....	473
Prof. H. Konen on the Distribution of Energy in the Spectra of Gases .....	475
Prof. O. W. Richardson on the Theory of Photoelectric and Photochemical Action .....	476
Sir E. Rutherford on the Structure of the Atom .....	488
Mr. C. G. Darwin on Collision of $\alpha$ Particles with Light Atoms. ....	499
Dr. N. Bohr on the Effect of Electric and Magnetic Fields on Spectral Lines .....	506
Prof. R. W. Wood: Separation of Close Spectrum Lines for Monochromatic Illumination. (Plate VII.) .....	524
Prof. R. W. Wood on the Production of a very intense Sodium Flame .....	530
Prof. R. W. Wood and Mr. W. P. Speas on a Photometric Study of the Fluorescence of Iodine Vapour.....	531
Proceedings of the Geological Society.....	538

## NUMBER CLX.—APRIL.

Prof. J. W. Nicholson on the High-frequency Spectra of the Elements, and the Structure of the Atom .....	541
Prof. E. Taylor Jones on Induction-Coil Potentials. (Plate VIII.).....	565

	Page
Dr. G. Hevesy on the Diffusion and Valency of the Radio-elements .....	586
Mr. S. Oba on the Absorption of $\gamma$ Rays .....	601
Mr. Harold G. Savidge on the Integration of a Class of Ordinary Linear Differential Equations of the Second Order .....	608
Mr. R. Hargreaves on Wien's Law .....	616
Prof. T. Godlewski on the Action of Colloids on Radio-active Products in Solution .....	618
Prof. E. C. C. Baly on Light Absorption and Fluorescence ..	632
Mr. A. O. Allen on the Slip-Curves of an Amsler Planimeter.	643
Messrs. W. Morris Jones and J. E. Malam on the Electrical Resistance of Nickel in Magnetic Fields .....	649
Dr. I. J. Schwatt on the Sum of an Infinite Series as the Solution of a Linear Differential Equation .....	659
Mr. W. H. Gibson on the Influence of Volume Change on the Fluidity of Mixtures of Miscible Liquids .....	662
Mr. J. Rose-Innes on the Integration of the Differential Equation applicable to a Plane Progressive Wave .....	669
Prof. A. W. Porter on the Formation of Images by means of an Opaque Disk. (Plate IX.) .....	673
Mr. C. G. Darwin on the Theory of X-Ray Reflexion.—Part II. ....	675
Mr. E. Marsden and Dr. P. B. Perkins on the Transformations in the Active Deposit of Actinium .....	690
Mr. H. G. J. Moseley on the High-Frequency Spectra of the Elements.—Part II. ....	703
Mr. Horace H. Poole on the Activity of freshly-formed Radium Emanation .....	714
Dr. S. A. Shorter on a Classification of Foaming Solutions ..	718
Dr. P. B. Perkins: A Determination of the Periods of Transformation of Thorium and Actinium Emanation....	720
Mr. W. A. Jenkins on the Effect of a Magnetic Field on Metallic Resistance. (Plate X.) .....	731
Mr. Gervaise Le Bas on the Theory of Molecular Volumes.—Part II. ....	740
Notices respecting New Books:—	
James Thomson's Collected Papers in Physics and Engineering .....	752
Department of Commerce; U.S. Coast and Geodetic Survey .....	752
Intelligence and Miscellaneous Articles:—	
British Association for the Advancement of Science: Committee for Radiotelegraphic Investigation—Special Investigation .....	753
On the Recombination of Ions made by $\alpha$ Rays, by R. D. Kleeman .....	755
On the Electrons liberated in Ionization, by R. D. Kleeman .....	755



## NUMBER CLXI.—MAY.

	Page
Sir J. J. Thomson on the Forces between Atoms and Chemical Affinity .....	757
Prof. J. S. Townsend and Mr. P. J. Edmunds on the Discharge of Electricity from Cylinders and Points .....	789
Mr. Harold Smith on the Spectroscopy of the Electric Brush Discharge in Weak Acids and Solutions. (Plate XI.) ..	801
Mr. E. Marsden on the Passage of $\alpha$ Particles through Hydrogen .....	824
Miss Margaret B. Moir on the Magnetic Properties of a Graded Series of Chrome Steels at Ordinary and Low Temperatures .....	830
Dr. C. V. Burton: An Experiment indicating that Matter takes up no Room in the $\text{\AA}$ ther.....	843
Sir Ernest Rutherford and Dr. E. N. da C. Andrade on the Wave-Length of the Soft $\gamma$ Rays from Radium B. (Plate XII.) .....	854
Dr. E. N. da C. Andrade on Regular Surface Markings in Stretched Wires of Soft Metals. (Plate XIII.) .....	869
Prof. H. L. Callendar on Thermodynamics of Radiation ...	870
Prof. W. H. Bragg on the Intensity of Reflexion of X Rays by Crystals .....	881
Prof. R. W. Wood and Mr. G. A. Hemsalech on the Fluorescence of Gases excited by Ultra-Schumann Waves. (Plates XIV. & XV.) .....	899
Dr. Manne Siegbahn on the Use of the Telephone as an Oscillograph. (Plate XVI.) .....	909
Intelligence and Miscellaneous Articles:—	
John Henry Poynting .....	914

## NUMBER CLXII.—JUNE.

Dr. R. D. Kleeman on the Disintegration of an Ion Cluster in a Gas under the Influence of an Electric Field .....	917
Dr. S. A. Shorter: Contribution to the Thermodynamical Theory of Ternary Mixtures.....	942
Mr. S. Smith on the Initial Stages of Ionization by Collision .....	963
Mr. Gervaise Le Bas on the Theory of Molecular Volumes.—Part III.....	976
Dr. G. A. Shakespear on some Modifications in an ordinary Balance which conduce to ease and quickness of weighing.	990
Mr. G. H. Livens on a Theory of the Rotational Optical Activity in Isotropic Media .....	994
Prof. R. W. Wood and M. G. Ribaud on the Magneto-optics of Iodine Vapour.....	1009
Prof. R. W. Wood and M. L. Dunoyer on the Separate Excitation of the Centres of Emission of the D Lines of Sodium. (Plate XVII.) .....	1018

	Page
M. L. Dunoyer and Prof. R. W. Wood: Photometric Investigation of the Superficial Resonance of Sodium Vapour. (Plate XVII. figs. 8 & 9.)	1025
Proceedings of the Geological Society	1035
Index	1038

## P L A T E S.

- I. Illustrative of Prof. H. Nagaoka and Mr. T. Takamine's Paper on Crossed Spectra obtained by Combinations of Different Interferometers, and their Applications to the Measurement of Difference in Wave-lengths.
- II. Illustrative of Mr. F. Soddy's Paper on the Existence of Uranium Y.
- III. Illustrative of Mr. C. W. H. Foord's Paper on Air-Pressures used in Playing Reed Instruments.
- IV. Illustrative of Mr. W. J. Walker's Paper on the Relationship between the Viscosity, Density, and Temperature of Salt Solutions.
- V. Illustrative of Prof. H. Nagaoka and Mr. T. Takamine's Paper on Anomalous Zeeman Effect in Satellites of Mercury Lines.
- VI. Illustrative of Dr. E. P. Kerschbaum's Paper on Interference Experiments in a Highly Rarefied Gas.
- VII. Illustrative of Prof. R. W. Wood's Paper on the Separation of Close Spectrum Lines for Monochromatic Illumination.
- VIII. Illustrative of Prof. E. Taylor Jones's Paper on Induction-coil Potentials.
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- X. Illustrative of Mr. W. A. Jenkins's Paper on the Effect of a Magnetic Field on Metallic Resistance.
- XI. Illustrative of Mr. H. Smith's Paper on the Spectroscopy of the Electric Brush Discharge in Weak Acids and Solutions.
- XII. Illustrative of Sir E. Rutherford and Dr. E. N. da C. Andrade's Paper on the Wave-Length of the Soft  $\gamma$  Rays from Radium B.
- XIII. Illustrative of Dr. E. N. da C. Andrade's Paper on Regular Surface Markings in Stretched Wires of Soft Metals.
- XIV. & XV. Illustrative of Prof. R. W. Wood and Mr. G. A. Hemsalech's Paper on the Fluorescence of Gases excited by Ultra-Schumann Waves.
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THE  
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[SIXTH SERIES.]

JANUARY 1914.



I. *The Temperature of Sublimation.* By J. JOLY, F.R.S.\*

IN the Philosophical Magazine for June 1913 I gave an account of experiments on the temperatures at which various sublimates are evolved from mineral substances. The sublimate was obtained by heating the powdered mineral on a platinum ribbon enclosed between watch-glasses, the approximate temperature of sublimation being ascertained in terms of the current heating the ribbon. The apparatus, which I have called the Apophorometer, is described in the *Phil. Mag.* for Feb. 1913.

Subsequently to the publication of my experiments on the temperature of sublimation, I received samples of several rare minerals through the kindness of the Trustees of the British Museum, of the Custodians of the Museum of Geology, Jermyn Street, and of the Oxford Museum. I have specially to thank, in connexion with these valuable contributions, Mr. G. Prior, Dr. H. H. Teall, and Professor Sollas. A few additional specimens were purchased. The object of this paper is to give an account of the results obtained on these specimens, in continuation of the results already published.

ANTIMONY.

In my former paper a table of results on antimony-bearing substances appears. It contains 20 experiments on substances containing the molecule  $\text{Sb}_2\text{S}_3$  and 5 on substances containing the antimony differently combined. Considering the former class of compounds first, the conclusion arrived

\* Communicated by the Author.

*Phil. Mag.* S. 6. Vol. 27. No. 157. Jan. 1914.

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at was that a compound of antimony of the form  $nRS$ ,  $mSb_2S_3$  becomes unstable in presence of oxygen at a temperature which is unaffected by the nature of  $R$  or by the value of  $n$  or  $m$ . In fact all these bodies give off their antimony at a temperature varying not very widely around  $480^\circ C$ . Judging from the five observations on other compounds of antimony, these bodies also break up near this temperature, whether sulphur is present or not.

The new results are as follows :—

TABLE I.  
 $nRS$ ,  $mSb_2S_3$ .

			$t^\circ$ .
1. Andorite.	$Ag_2S$ , 2 $PbS$ , 3 $Sb_2S_3$ .	Oruro.....	510
2. Kermesite.	$Sb_2O_3$ , $Sb_2S_3$ .	Loc. ?.....	430
3. Polybasite.	9 $Ag_2S$ , $Sb_2S_3$ .	Loc. ? .....	430
4. Livingstonite.	$HgS$ , 2 $Sb_2S_3$ .	Tasco.....	430
5. Nagyagite.	$Au_2Pb_{14}Sb_3Te_7S_{17}$ .	Nagyag .....	485
6. Kilbrickenite.	6 $PbS$ , $Sb_2S_3$ .	Kilbricken .....	430
7. Tetrahedrite.	4 $Cu_2S$ , $Sb_2S_3$ .	Botes.....	460
8.	" "	Westerwald .....	550
9.	" "	Kapnik .....	530
10.	" "	Pribram .....	590

As stated in the first paper, antimony may sublime as the tetroxide  $Sb_2O_4$  or as antimonious oxide  $Sb_4O_6$ . The former sublimate is insoluble in cold  $HCl$ , the latter is instantly soluble. The earlier experiments seemed to show that the sublimate  $Sb_4O_6$  appeared at a lower temperature than  $Sb_2O_4$  and, hence, was that which generally marked the beginning and lowest temperature of decomposition. Repeated and careful observations have, however, failed to substantiate this point. Comparison of very many results showed that in successive experiments on the same powder small traces of either oxide might first appear or both appear together.

A mixture of galena and bi-smuth ground together in the agate mortar and in the proportions required to represent the composition of zinkenite ( $PbS$ ,  $Sb_2S_3$ ), behaved in all respects identical with the mineral zinkenite. Similarly argentite and stibnite mixed to represent the composition of miargyrite ( $Ag_2S$ ,  $Sb_2S_3$ ) showed no difference in behaviour from the latter mineral.

It will be seen that the results of Table I. agree with those already published.

#### ARSENIC.

The subdivision of the arsenic-bearing minerals into three groups according to the temperature at which the arsenic is yielded, as suggested in the first paper, is supported by the more recent experiments.



As nothing has been said in the first paper as to the characters and recognition of the sublimate of  $\text{As}_2\text{O}_3$ , a word on the subject may be useful here. The sublimate is always very nebulous and diffusive in character; never pure white, but greivish; or even brownish if the oxidation is imperfect. It begins as a mere dulling of the glass. Seen under the microscope it may show perfect, colourless octahedra, especially on the lower glass, if slowly formed; or it may appear as a formless dust. From the latter, crystals may be obtained by reheating the sublimate between the glasses. The smell of garlic is rarely obtained under the conditions. When tested for odour there is a faint earthy smell. It is less easily volatilized off the glass than sulphur. It is imperfectly soluble in cold  $\text{HCl}$ ; more readily soluble in warm  $\text{HCl}$ , and easily soluble in hot water. The solution in hot water may be tested readily by any of the usual chemical tests.

The following results are additional to those already published:—

TABLE II.

III.  $\text{RAs}$ ;  $\text{RAsS}$ ;  $\text{R}_2\text{As}_3$ ;  $\text{R}_3\text{As}_4$ ;  $\text{RAs}_2$ .

			$t^\circ$ .
1.	Glauco-dote. $(\text{CoFe})\text{AsS}$ .	Tunaberg .....	480
2.	" "	Loc. ? .....	480
3.	Gersdorffite. $(\text{NiCoFe})_3(\text{AsS})_4$ .	Müsen .....	450
4.	" "	Loc. ? .....	480
5.	Breithauptite. $\text{NiSb}$ with tr. of $\text{As}$ .	Loc. ? .....	520
6.	Tennantite. $11 \text{ CuS}$ , $\text{FeS}$ , $5 \text{ CuAsS}$ .	Cornwall .....	500
7.	Ullmannite. $\text{NiS}_2$ , $\text{Ni}(\text{SbAs})_2$ [? No $\text{Sb}$ detected].	Lobenstein .....	530
8.	Alloclasite. $\text{Co}(\text{AsBi})\text{S}$ .	Loc. ? .....	480
9.	Domykite. $\text{Cu}_3\text{As}$ .	Paracatas .....	370
10.	" "	Loc. ? .....	365
11.	Algodonite. $\text{Cu}_6\text{As}$ .	Mohawk Mine .....	350
12.	Whitneyite. $\text{Cu}_9\text{As}$ .	Houghton Co. ....	395

II.  $\text{RS}$ ,  $\text{As}_2\text{S}_3$ ;  $\text{As}_2\text{S}_3$ ;  $\text{RAs}_3$ ;  $\text{RAs}_2\text{S}_5$ .

13.	Enargite. $3 \text{ Cu}_2\text{S}$ , $\text{As}_2\text{S}_3$ .	Red Mt., Colorado ...	290
14.	" "	Loc. ? .....	290
15.	Allemontite. $\text{SbAs}_3$ .	Allemont .....	250
16.	" "	" .....	200
17 & 7.	Ullmannite. Considerable subl. of $\text{As}_2\text{O}_3$ at	.....	285

I.  $\text{As}$ ;  $\text{AsS}$ ; loosely attached  $\text{As}$ .

18.	Geocrinite. Sala, tr. of $\text{As}_2\text{O}_3$ at	.....	150
19, 17 & 7.	Ullmannite. " " "	.....	185
20 & 2.	Glauco-dite. " " "	.....	190

In my former paper I remarked with reference to group III. of the Table that, owing to the results then obtained being mainly confined to iron, nickel, and cobalt compounds, we were not in a position to examine into the possible influence of the atomic weight of the stable element present, and I drew attention to the rather anomalous indication of domykite. In the present list it will be seen that two other copper arsenides support the position of domykite. It is to be remarked that the somewhat higher decomposition point of whitneyite is probably in part due to the coarser grain of the powder used; the ductile nature of this substance rendering pulverization impossible. It can only be powdered by abrasion. From these results it would appear as if the stable element present was not without some effect on the temperature of sublimation.

Some analyses carried out on the apophorometer, bearing upon the formulæ to be ascribed to some of the minerals examined, may now be given.

Primarily there is the question, which I raised in my former paper, as to where arsenides of the composition  $RA_s_2$  should be placed in the Table. A smaltite of Schneeberg was carefully examined:—

*Analysis 1. Smaltite; Schneeberg, Saxony.* Weight taken 13·6 mgrms. Total  $As_2O_3$  up to white heat  $13\cdot0 = 9\cdot8$  mgrms. As. Residue 4·5 mgrms.

The Schneeberg mineral, according to Hintze, is mainly a nickel chloanthite with  $As=77$ ;  $Co=3$ ;  $Ni=12$ ;  $S=1$  or less. The residue in the present experiment gave a vivid blue bead with borax, but it does not much matter for the purpose of the experiment whether we calculate it as  $NiO$ ,  $Co_3O_4$ , or  $Fe_2O_3$ . The first gives 3·6 Ni; the second 3·4 Co; the third 3·7 Fe. I take 3·6 (Ni, Co, Fe). This makes the added weights 13·4. The deficit is about 1·5 per cent. and is probably S.

Hence,  $As=72\cdot0$ ;  $(Ni, Co, Fe)=26\cdot5$ ;  $S=1\cdot5$ . And the relative number of atoms—As 96; (Ni, Co, Fe) 45 (about)—leaves little doubt that the formula is essentially  $(Ni, Co, Fe) As_2$ .

Now in the experiment the  $As_2O_3$  was evolved as follows:—

0·5 mgrms.	at 230– 320.	Group II.
9·4     ,,     ,,	420– 540.	,,   III.
1·0     ,,     ,,	660– 760.	
0·5     ,,     ,,	920–1450 (?)	
1·6     ,,     ,,	full white heat.	

The decomposition is, it will be seen, for the most part effected within the temperature range of group III. It is probable that the liberation of As below this is referable to the presence of the molecule  $\text{As}_2\text{S}_3$  in subordinate amount, accounting for the S present and the slight excess of As. The composition is, however, essentially that of a diarsenide, and the break up of this molecule must be referred to the temperature range of group III.

The position in the scale of temperature of the intervals of stability and instability appear to be only roughly definable even on successive experiments on the same powdered material. The temperature at which an interval of decomposition or instability comes to an end depends to some extent, apparently, on the duration of heating at the lower temperatures embraced by the interval. Thus the temperature  $320^\circ$  which marks the conclusion of an interval of instability, as recorded above, on another experiment was found to be some 30 degrees lower; the heating at the lower part of the interval having been much more prolonged. The temperature of commencing instability,  $230^\circ$ , was, however, the same in each experiment. Similarly the second interval of instability began at temperatures which were found to be fairly concordant. The upper successive nodes and internodes seemed less well defined, but their position on the scale of temperature cannot be investigated without special precautions to secure uniform increase of temperature and continuous observation of sublimation.

With regard to the cause of these successive intervals of stability and instability, it seems probable that the interval  $230^\circ$ – $320^\circ$ , which covers that of group II., indicates the presence of the  $\text{As}_2\text{S}_3$  molecule, the existence of which is, also, to be inferred from the analysis. Over the next interval the diarsenide molecule breaks up. From its relatively large amount it is not probable that this constituent is in any way generated by rearrangements attending the evolution of arsenic at the lower temperature. It is, however, quite possible that rearrangements attending the break up of the diarsenide molecule are responsible for the cessation of instability, the succeeding interval of stability, and for the decomposition which follows this interval. The firm retention of a considerable part of the volatile element till a very high temperature is attained, strongly suggests the formation of a compound or alloy of the residual arsenic with the stable element; this compound possessing a very high degree of stability.



*Analysis 2. Chloanthite* (cited as smaltite and numbered 19 in Table II. of paper in Phil. Mag. p. 861, June 1913).

An analysis on the apophorometer gave the following results :—

Wt. taken 10.9 mgrms. This yielded 0.55 mgrm. arsenic in group II., heating for 60 minutes at  $255^{\circ}$ ; and 6.51 mgrms. arsenic over the interval  $400^{\circ}$  to white heat. The residue showed but little cobalt and weighed 4.3 mgrms. If its composition be assumed to be NiO, the deficit on the added weighings is 0.39 mgrm., which is accounted for by the observed evolution of a little sulphur. The percentages are As 64.2; Ni 31.7. The observations show that the more stable molecule yielded 5.4 mgrms. As. Assigning the whole of the Ni to it we get as its composition  $\text{Ni}_3\text{As}_4$ , very nearly. The molecule breaking up in group II. is probably  $\text{As}_2\text{S}_3$ , and the complete formula approximates to  $\text{As}_2\text{S}_3 \cdot 5 (\text{Ni}_3\text{As}_4)$ .

*Analysis 3.* A partial re-analysis of the *rammelsbergite*, appearing in Table II. of the former paper as No. 15, was made.

Wt. taken 10.6 mgrms. No sublimate was obtainable till over  $500^{\circ}\text{C}$ . Between  $500^{\circ}$  and  $700^{\circ}$ , 7.6 mgrms. of  $\text{As}_2\text{O}_3$  were taken off. At a white heat a further 0.7 mgrm. was evolved. These sublimates contain 6.2 mgrms. As. The residue seemed to be mainly NiO and weighed 5.3 mgrms., containing 4.25 mgrms. Ni. Total weight accounted for 10.44; deficit 0.16. From the result As 59.6 per cent.; Ni 41.3 per cent., the atomic ratios are As 79, Ni 69. If (as is probable) Ni is a little over-estimated and we take the ratio as 80:60 the formula  $\text{Ni}_3\text{As}_4$  is derived. The result formerly arrived at and given *loc. cit.* p. 864, was As 58 per cent., Ni 38 per cent., giving  $\text{Ni}_3\text{As}_4$  as above. The analyses, therefore, agree.

In the former paper  $\text{RAs}_3$  was placed provisionally in group II. There was then no direct experimental evidence in support of this assumption. Recent observations on two allemontites ( $\text{SbAs}_3$ ) from Allemont showed that the evolution of  $\text{As}_2\text{O}_3$  began at  $200^{\circ}$  closely in both cases. This is evidence in favour of the position assigned to the tri-arsenide molecule.

#### SULPHUR.

At a low temperature sulphur yields a sublimate of the element which under the microscope is found to consist of highly refracting globules. At higher temperatures it is

oxidized and passes off as a gas. It may at these temperatures unite with the water present between the glasses and condense on the latter as a very acid liquid. The presence of sulphur is often revealed by faint whirling clouds, taking various spiral forms of much regularity, and doubtless composed of particles of condensed vapour. These whirling clouds are almost characteristic of this element. The earliest appearance of sulphur being a mere dulling of the glass may easily be mistaken for arsenic unless tests be applied as described in the former paper (*loc. cit.* p. 866).

The following Table contains a revision of the earlier data and additional results:—

TABLE III.

		<i>t</i> °.
1. Molybdenite. $\text{MoS}_2$ .	Loc. ? .....	450
2. Pyrites. $\text{FeS}_2$ .	„ .....	450
3. Marcasite. „	Jasper Co. ....	440
4. Hauerite. $\text{MnS}$ .	Radusa .....	450
5. Stannite. $\text{Cu}_2\text{S}$ , $\text{FeS}_2$ , $\text{SnS}_2$ .	St. Agnes .....	460
6. Chalcopyrite. $\text{Cu}_2\text{S}$ , $\text{Fe}_2\text{S}_3$ .	Loc. ? .....	470
7. Chalcosite. $\text{Cu}_2\text{S}$ .	Cornwall .....	490
8. Linnaeite. $\text{CoS}$ , $\text{Co}_2\text{S}_3$ .	Mussen .....	480
9. Sphalerite (5). $\text{ZnS}$ .	Various.....	500–510
10. Pentlandite. $2\text{FeS}$ , $\text{NiS}$ .	Lillehammer.....	480
11. Covellite. $\text{CuS}$ .	Butte.....	400
12. Galenite. $\text{PbS}$ .	Loc. ? .....	470
13. Bornite. $\text{Cu}_2\text{S}$ , $\text{CuS}$ , $\text{FeS}$ .	Audley Mine, Cork ...	430
14. Kilbrickenite. $6\text{PbS}$ , $\text{Sb}_2\text{S}_3$ .	Kilbricken.....	440
15. Argentite. $\text{Ag}_2\text{S}$ .	Joachimsthal .....	460
16. Zinkenite. $\text{PbS}$ , $\text{Sb}_2\text{S}_3$ .	Wolfsberg.....	400
17. Nagyagite. $\text{Au}_2\text{Sb}_3\text{Pb}_{14}\text{Te}_7\text{S}_{17}$ .	Nagyag .....	420
18. Galenobismutite. $\text{PbS}$ , $\text{Bi}_2\text{S}_3$ .	Nordmarken.....	470
19. Alloclasite. $\text{Co}(\text{AsBi})\text{S}$ .	Loc ? .....	440
20. Aikinite. $3(\text{PbCu}_2)\text{S}$ , $\text{Bi}_2\text{S}_3$	„ .....	420
21. „ „	Beresowsk, Ural .....	440
22. Emplectite. $\text{Cu}_2\text{S}$ , $\text{Bi}_2\text{S}_3$ .	Schneeberg .....	400
23. „ „	Schwarzenberg .....	470
24. Bismuthenite. $\text{Bi}_2\text{S}_3$ .	Schneeberg .....	400
25. Stibnite. $\text{Sb}_2\text{S}_3$ .	Iyo, Japan .....	380
<hr/>		
26 & 16. Zinkenite .....		130
27 & 14. Kilbrickenite .....		185
28. Sternbergite. $\text{Ag}_2\text{S}$ , $\text{Fe}_4\text{S}_5$ .	Königsberg .....	170
<hr/>		
29 & 4. Hauerite .....		70
30 & 28. Sternbergite.....		70
31. Flowers of Sulphur .....		65–70



The Table shows that sulphur is generally liberated from the metallic sulphides between  $440^{\circ}$  and  $480^{\circ}$ . Certain of the minerals examined, *i. e.* bauerite, kilbrickenite, and zinkenite, liberated a part of their sulphur at a lower temperature. Generally, this sulphur was little more than a trace. In the case of the kilbrickenite, however, the low-temperature sublimate of sulphur amounted to 5 per cent. by weight of the mineral after prolonged heating at  $185^{\circ}$ . This is nearly one-third of the sulphur present.

#### TELLURIUM.

Only 7 tellurides had been examined at the time of writing the first paper. Those few results appeared to indicate that the tellurides were divisible into groups according as the molecule is of the structure  $R\text{Te}$  or  $R\text{Te}_2$ . This view is sustained by the additional observations now available.

I may recall that the presence of tellurium may be indicated by a black sublimate,  $\text{TeO}$ , which is peculiar to tellurides breaking up at a relatively low temperature (about  $500^{\circ}$ ) or by a white sublimate which is only formed at a higher but rather variable temperature:— $600^{\circ}$  to  $900^{\circ}$ . The white sublimate has the composition  $\text{TeO}_2$ . Tellurides which first break up at the higher temperature only show the white sublimate. Those which become unstable at the lower temperature give the black sublimate, and if the temperature be then raised, the white sublimate also. The more stable tellurides possess the structure  $R\text{Te}$ ; the less stable the structure  $R\text{Te}_2$ , or  $R\text{Te}_3$ . Hence these two classes may be at once identified by the colour of the sublimate first given off on gradually heating them on the apophorometer.

TABLE IV.

		$R\text{Te}$ .	$i^{\circ}$ .
1. Altaite.	$\text{PbTe}$ .	Las Cruces .....	$\text{TeO}_2$ 850
2. "	"	" .....	" 820
3. "	"	Loc. ? .....	" 710
4. Hessite.	$\text{Ag}_2\text{Te}$ .	Altai .....	" 900
5. "	"	" .....	" 820
6. "	"	Sardinsky Mine, Altai .....	" 930
7. Petzite.	$(\text{AuAg})\text{Te}$ .	.. .....	" 750

		RTe <sub>2</sub> ; RTe <sub>3</sub> ; Te.	t°.
8.	Calaverite. (AuAg)Te <sub>2</sub> .	Kalgoorlie.....	TeO 450; TeO <sub>2</sub> 675
9.	" "	Cripple Creek ...	" 520; " higher
10.	" "	.....	" 530; " 600
11.	"Petzite"(?). PbTe <sub>3</sub> .	Red Cloud Mine.	" 460; " 900
12.	Tetradymite. Bi <sub>2</sub> Te <sub>3</sub> .	Hungary.....	" 460; " 750
13.	" "	Schonbkaw, Scheennitz.	" 480; " 750
14.	Nagyagite. Au <sub>2</sub> Pb <sub>14</sub> Sb <sub>3</sub> Te <sub>7</sub> S <sub>17</sub> .	Nagyag .....	" 440; " 610
15.	" "	" .....	" 525; " 610
16.	Sylvanite. AuAgTe <sub>4</sub> .	.....	" 460; " 770
17.	" "	Loc. ? .....	" 480; " 780
18.	" "	Kalgoorlie .....	" 520; " 730
19.	Coloradoite. HgTe.	" .....	" 520; " 835
20.	Native Tellurium.	Facebay, Tran- sylvania.	" 525; " 850
21.	Tellurium, prepared.	.....	" 525; " 850
22.	" "pure."	.....	" 470; " 700

Two substances in this Table require special notice. No. 10 was obtained by purchase and reached me labelled "Petzite." On obtaining the result recorded in the table, it was concluded that the identification must be in error. Petzite is a monotelluride of gold and silver. As such it should first yield the white sublimate of TeO<sub>2</sub>. A rough quantitative analysis on the apophorometer was made. A very high percentage of tellurium was arrived at—nearly 80 per cent. Some oxide of lead was, however, included, an excessive temperature having been employed. Mr. J. R. Cotter was so good as to make for me a quantitative analysis in the ordinary way. The result was:—

Tellurium.....	57.54
Lead.....	33.70
Iron .....	1.22
Insol. in HNO <sub>3</sub> ...	8.77

The insoluble part was found to contain an amount of gold equal to 0.47 per cent. of the mineral. The balance was insoluble in aqua regia, and was determined as mainly silica: evidently an impurity. Silica is visibly associated with the mineral.

An earlier analysis gave Mr. Cotter a slightly larger percentage of tellurium.

The density taken on a clean homogeneous fragment was found to be 6.55.

The mineral is certainly not petzite. The latter body has the composition  $\text{AuTe}$ ,  $3\text{AgTe}$ , and a density of 8.7–9.0. The analysis suggests  $\text{PbTe}_3$  as being approximately the composition of the telluride. It may be a new species.

The second telluride calling for notice is No. 18. This substance, on its chemical composition, should not give the low-temperature sublimate. That it does so may, perhaps, be ascribed to the large amount of the very volatile element combined with the tellurium.

#### BISMUTH.

Four oxides are observed. (1) The bismuthous oxide, the most stable oxide, is plentifully obtained as a sublimate at high temperatures. If a little of it is scraped from the glass and heated on the hob, it will be found to fuse at about  $900^\circ$  and volatilize at about  $1010^\circ$ . As evolved from the element or from compounds, a higher temperature is generally required in order to obtain the sublimate: from  $1200^\circ$  to  $1300^\circ$ . It is gradually formed on the hob as the substance decomposes or oxidizes. Thus, if pure elemental bismuth is treated, the metal undergoes colour changes from yellow to orange, red, ash-red, to purple. At a little over  $900^\circ$  there is fusion of the oxide, and at a temperature rather over  $1200^\circ$  the sublimate is obtained.

The sublimate is canary-yellow to pale whitish-yellow or nearly white in colour. It is nebulous and hazy in form; never definite and streaky when formed as described. Under the microscope it is granular. It is non-volatile and is soluble in  $\text{HCl}$ , but not soluble in strong solution of  $\text{KHO}$ .

This oxide may appear in small traces at a lower hob-temperature if there is deflagration or sudden decomposition of the mineral. It then takes a well-defined form, reproducing the chance pattern of the deposit on the hob. The sudden high temperature developed on deflagration may be responsible for its sudden and limited development. It is whitish in colour and shows the same physical and chemical properties described above. It has been obtained from colloidal bismuth at  $640^\circ$ ; from emplectite at  $600^\circ$ ; from cosalite and tetradymite at about  $700^\circ$ ; from aikinite at from  $510^\circ$  to  $690^\circ$ . Heating may, in many cases, be so carefully regulated that deflagration is avoided, and in these cases the bismuthous oxide is only obtained at the usual high temperature. In quantitative work the low-temperature evolution of the oxide is so limited in amount as to render it unimportant.



(2) With native bismuth and some samples of chemically prepared bismuth as well as with some mineral compounds of bismuth, there appears a whitish-buff or yellowish-buff sublimate, very nebulous and diffusive, at temperatures which seem variable but are always lower than that of the formation of the normal sublimate of  $\text{Bi}_2\text{O}_3$ . It may be evolved at the moment of sudden decomposition when the internal temperature of the particles is unknown.

This body seems to be undoubtedly an oxide of bismuth; the test with  $\text{SnCl}_2$  in every case giving the characteristic blackish-brown precipitate. A borax bead fed with the scraped-up sublimate is yellow hot and colourless cold in the oxidizing flame.

The distinctive feature of this oxide is its volatility. It is readily volatile off the glasses. Heated between them it forms smoky clouds which may condense to minute colourless and transparent regular octahedra. In general the sublimate is merely granular, as seen under the microscope. It is heavy and often falls into the lower glass.

It is instantly soluble in dilute  $\text{HCl}$ , in aqua regia, and in solution of  $\text{KHO}$ . It is slowly or doubtfully soluble in  $\text{HNO}_3$ . With elemental bismuth it has been obtained at  $245^\circ$  to  $345^\circ$ ; soon ceasing to come off. With native bismuth it was obtained from  $470^\circ$  to  $630^\circ$ ; more generally near the latter temperature. By raising the temperature very gradually it was found—at least in the case of elemental bismuth—that the formation of this oxide was preventable; the stable bismuthous oxide being formed on the hob and ultimately sublimed. From aikinite this volatile oxide was got at  $600^\circ$  and  $820^\circ$ . From bismuthenite it was obtained at  $510^\circ$ – $600^\circ$ .

The observations do not indicate that any importance attaches to this oxide in quantitative work, as, relatively to the stable, high-temperature oxide, it is small in amount. In many cases it does not appear to be formed. I have not identified it with any recorded oxide of bismuth of which I am aware.

(3) The bismuthine oxide;  $\text{Bi}_2\text{O}_5$ (?). Along with the high-temperature sublimate of  $\text{Bi}_2\text{O}_3$ , reddish and pink streaks are sometimes observed. This is a non-volatile sublimate: insoluble in  $\text{HCl}$ , so that it remains after the accompanying  $\text{Bi}_2\text{O}_3$  is dissolved. It may be the oxide  $\text{Bi}_2\text{O}_5$ . It is said to pass to  $\text{Bi}_2\text{O}_3$  if heated in air at  $305^\circ$ . This has not been observed in the present case. It is not important in analysis, being very small in amount.

(4) Hypobismuthous oxide,  $\text{Bi}_2\text{O}_2$ . The black oxide is

obtainable from colloidal bismuth, attending deflagration. It is not volatilized off the glasses and is insoluble in  $\text{HCl}$  or in solution of  $\text{KHO}$ . It whitens slowly when heated on the glass.

The test by chloride of tin is the best for bismuth under the conditions obtaining in these experiments. Put a drop or two of solution of  $\text{SnCl}_2$  on the sublimate, followed by a couple of drops of dilute  $\text{HCl}$ , and work round with a stirring-rod till all is dissolved. Add now a little  $\text{NH}_4\text{HO}$  solution, or  $\text{KHO}$  solution, till the first formed white precipitate is dissolved. The ppt. of  $\text{Bi}_2\text{O}_3$  then slowly collects.

If the sublimate is soluble in  $\text{KHO}$  sol., it is even more effective to add a little of this and then drop in a few crystals of  $\text{SnCl}_2$ ; these only partially dissolve and rapidly blacken, bringing down the black oxide. This black precipitate will be found to whiten in a few hours if left exposed to the air.

TABLE V.

1. Native Bismuth. Volatile, buff-yellow subl. at  $470^\circ$ : subl. of  $\text{Bi}_2\text{O}_3$  at white heat.
2. Bismuthenite.  $\text{Bi}_2\text{S}_3$ . Schneeberg. Volatile subl. at  $500^\circ$ – $600^\circ$  with deflagration; subl. of  $\text{Bi}_2\text{O}_3$  at white heat.
3. Galenobismutite.  $\text{PbS}$ ,  $\text{Bi}_2\text{S}_3$ . Nordmarken. Tr. of  $\text{Bi}_2\text{O}_3$  with deflagration at  $560^\circ$ ; and at high temperature.
4. Cosalite var. Bjelkite.  $2\text{PbS}$ ,  $\text{Bi}_2\text{S}_3$ . Bjelke Mine. Tr. of  $\text{Bi}_2\text{O}_3$  with deflagration at  $720^\circ$ ; and at white heat.
5. Lillianite.  $3\text{PbS}$ ,  $\text{Bi}_2\text{S}_3$ . Lillian Mine, Leadville. The high temp. subl. of  $\text{Bi}_2\text{O}_3$  only observed.
6. Aikinite.  $3(\text{Pb}, \text{Cu})\text{S}$ ,  $\text{Bi}_2\text{S}_3$ . Loc.?. Tr. of  $\text{Bi}_2\text{O}_3$  with deflag. at  $510^\circ$ ; Tr. of vol. white subl. at  $600^\circ$ ;  $\text{Bi}_2\text{O}_3$  at high temperature.
7. „ Beresoff, Siberia. Tr. of  $\text{Bi}_2\text{O}_3$  at  $620^\circ$  with deflag. and at high temperature.
8. „ Loc.?. Tr. of  $\text{Bi}_2\text{O}_3$  with deflag. at  $670^\circ$ ; Tr. of vol. white subl. at  $820^\circ$ .  $\text{Bi}_2\text{O}_3$  at high temp.
9. Emplectite.  $\text{Cu}_2\text{S}$ ,  $\text{Bi}_2\text{S}_3$ . Schwarzenberg. Tr. of  $\text{Bi}_2\text{O}_3$  at  $600^\circ$  with deflag.; and at  $1200^\circ$ .
10. Tetradymite.  $\text{Bi}_2\text{Te}_3$ . Schemnitz.  $\text{Bi}_2\text{O}_3$  at white heat.
11. Alloclasite.  $\text{Co}(\text{As}, \text{Bi})\text{S}$ . Loc.?.  $\text{Bi}_2\text{O}_3$  at  $1350^\circ$  with red streaks.

In the case of the sulphobismuthites the high temperature at which the sublimate of the oxide appears in bulk does not define the decomposition point of the mineral, but only that at which the oxide itself becomes volatile. The oxide is, in fact, formed at some lower temperature, collecting upon the hob while other volatile constituents pass off, and remaining

there unless the temperature is finally raised to about  $1200^{\circ}$  or even higher. The actual decomposition of the mineral is often defined by the appearance of deflagration at some lower hob-temperature, varying from about  $600^{\circ}$  to  $700^{\circ}$ .

All the substances 2 to 9 contain the molecule  $\text{Bi}_2\text{S}_3$ . These appear to break up at temperatures varying around  $600^{\circ}$ ; lillianite alone of these bodies showing no low temperature sublimate.

#### SELENIUM.

Only one oxide,  $\text{SeO}_2$  is recorded. It forms a diffusive, white, sublimate possessing a more or less acicular structure as seen under the microscope. It is very volatile, clearing rapidly off the upper glass just over the heated platinum; and leaving selenium behind it if any of the element has been volatilized without oxidation. The sublimate of the oxide is very hygroscopic, the crystals melting when breathed upon and being replaced by wet patches.

Compounds in which selenium is loosely attached give much red sublimate of selenium at low temperatures. With native selenium it is difficult to get the oxide in any quantity. The red sublimate begins at about  $300^{\circ}$  and the white at about  $440^{\circ}$ . Presence of oxygen favours the formation of the red sublimate, although this does not appear to contain any appreciable quantity of oxygen. In an atmosphere of oxygen selenium may be sublimed entirely in the form of the red sublimate without any gain in weight being detectable. Thus 14.5 mgrms. of selenium sublimed at  $460^{\circ}$  in oxygen showed not the smallest increase in weight. In coal-gas selenium sublimes as a rich black sublimate.

The first appearance of a sublimate from a selenium compound is often that of a pale reddish film, best seen by placing the glass on white paper. The film is dichroic, passing a fine green sheen, like certain aniline dyes. To the touch this film feels sticky: gentle rubbing appears to intensify the sheen.

In quantitative work careful regulation of the temperature will enable nearly all the selenium to be got off as the oxide. Thus clausthalite yields at  $340^{\circ}$  a faint trace of red sublimate, but if raised to  $600^{\circ}$  the white sublimate begins to form, and between  $700^{\circ}$  and  $850^{\circ}$  all selenium is got off as  $\text{SeO}_2$ , massicot only being left, which does not sublime till about 100 degrees higher.



The following selenium compounds have been examined:—

## TABLE VI.

Berzelianite, $\text{Cu}_2\text{Se}$ .	Strikerum Mine, Småland.
	White sublimate at $440^\circ$ .
Eucairite, $\text{Cu}_2\text{S}$ , $\text{Ag}_2\text{Se}$ .	Loc. as above.
	Tr. of red subl. at $380^\circ$ .
	White subl. at $410^\circ$ .
Clausthalite, $\text{PbSe}$ .	Tilkerode; Harz.
	Tr. of red subl. at $340^\circ$ .
	White subl. at $600^\circ$ .

## LEAD.

The sublimate formed in air is  $\text{PbO}$ . It forms a yellowish sublimate which shows bluish-white where it thins out on the margins. The yellow colour intensifies upon heating. Owing to its high specific gravity much of it falls into the lower glass. Under the microscope it is finely granular. It is soluble in solution of  $\text{KHO}$  and in  $\text{HCl}$ .

The formation of this sublimate is at a higher temperature than that at which the mineral breaks up. Massicot, as an olive-yellow slag, first forms gradually on the hob as the mineral decomposes. This melts at about  $930^\circ$ , sublimation beginning at a temperature approximating to  $1000^\circ$ , when it progresses steadily. The sublimate is, therefore, obtained below the temperature of volatilization of  $\text{Bi}_2\text{O}_3$  and above that of  $\text{TeO}_2$ , but unless the temperature be carefully attended to there is risk of lead oxide volatilizing along with the latter sublimate.

Iveagh Geological Laboratory.

II. *On the Interaction between Radiation and Free Electrons.*

By J. H. JEANS, M.A., F.R.S.\*

1. **T**HERE is now very general agreement that for a system of matter and æther to give Planck's formula for the radiation in its final steady state, the motion of the system must be in some way different from that predicted by the classical laws of dynamics as summarized in the principle of Least Action.

The problem of finding a new system of laws which shall lead to Planck's formula is as yet unsolved. In our present state of knowledge the problem is largely one of guessing, and the lucky guess has not yet been made. On the other

\* Communicated by the Author.

hand, a problem which admits of scientific and ordered treatment is the following: to examine at what exact point or points it is necessary to break with the old dynamics in order to obtain Planck's formula for the final partition of radiant energy.

To begin with, there is nothing incompatible with Planck's formula in the classical laws of propagation of light in free æther. It is well known that the partition of energy is not changed by propagation in free æther—any law of partition persists indefinitely so long as no interaction between æther and matter occurs. Stated analytically, the argument runs as follows:—If  $F(\lambda, T)d\lambda$  is an initial partition of energy, then the final law is  $F(\lambda, T)d\lambda$  also, and since this is general enough to include Planck's law, no break need be made with the old dynamics as regards propagation in free æther.

Next, there is nothing incompatible with Planck's formula in the classical laws of thermodynamics as applied to radiant energy. For according to these laws, if  $F(\lambda, T)d\lambda$  is the initial partition of energy, the final law, after an infinite number of thermodynamical processes, can be shown to be of the form  $\phi(\lambda T)\lambda^{-5}d\lambda$  (Wien's law), in which  $\phi$  is a function which cannot be determined by purely thermodynamical reasoning. Since this final law is general enough to cover Planck's law, we may conclude that there is nothing in the thermodynamical theory of radiation which is incompatible with Planck's law. Thus Planck's law in no way compels us to abandon the classical laws of either propagation or of reflexion, compression, &c. of radiation, so long as these latter processes are effected by ideal walls such as are imagined in thermodynamics. The classical laws may stand for free æther and for ideal matter: it is when we come to real matter that the break with the classical laws must be made if we are to arrive at Planck's formula.

In the present paper an attempt is made to carry the investigation further along these lines. The simplest system of real matter which can be imagined is a single electron. I have tried to examine whether there is anything inconsistent with Planck's law in the classical laws of interaction between radiant energy and a single free electron. To answer this, it is necessary to investigate what would be the final law of partition of radiant energy in a system in which the radiant energy started from any initial law of partition, and had this law modified by encounters with a single free electron, the laws of interaction being assumed to be the classical laws. The question is: Will the final law be general enough to include Planck's law?

2. A single ray of light propagated parallel to the axis of  $x$  may be taken to be given by

$$\begin{aligned} X=0, \quad Y=A \cos \kappa(x+Vt), \quad Z=0, \\ \alpha=0, \quad \beta=0, \quad \gamma=-A \cos \kappa(x+Vt). \end{aligned}$$

The equations of an electron moving freely in this field according to the classical laws, will be

$$\begin{aligned} m\ddot{x} &= -eA \frac{\dot{y}}{V} \cos \kappa(x+Vt) + \left[ \frac{2}{3} \frac{e^2}{V^3} \ddot{x} + \dots \right] \\ m\ddot{y} &= eA \cos \kappa(x+Vt) + eA \frac{\dot{x}}{V} \cos \kappa(x+Vt) + \left[ \frac{2}{3} \frac{e^2}{V^3} \ddot{y} + \dots \right] \\ m\ddot{z} &= \left[ \frac{2}{3} \frac{e^2}{V^3} \ddot{z} + \dots \right], \quad \dots \dots \dots (1) \end{aligned}$$

in which the terms in square brackets represent the retarding force on the electron produced by its own emission of radiation. If the frequency of the light is  $p$ , so that  $p=\kappa V$ , the ratio of these terms to those on the left-hand sides of the equations is of the order of magnitude  $\frac{2}{3} \frac{e^2}{mV^3} p$ . Giving to  $m$  its electromagnetic value  $\frac{2}{3} \frac{e^2}{aV^2}$ , this ratio is equal to  $pa/V$  or  $2\pi a/\lambda$ .

We are searching for the point of departure between the true laws and the classical laws, and this departure is known, from observation, to be most pronounced at low temperatures, at which all the radiation is of great wave-length, and the motion of free electrons is very slow. We may accordingly limit ourselves to the consideration of the problem for low temperatures, in the certainty that if a break with the classical laws is necessary, this special problem will disclose it. This limitation makes it legitimate to neglect  $a/\lambda$ , and therefore to omit all the terms in square brackets in the above equations. Further, it permits us to disregard variation of mass with velocity, and so to treat  $m$  as constant.

The equations simplified in this way become

$$\left. \begin{aligned} m\ddot{x} &= -eA \frac{\dot{y}}{V} \cos \kappa(x+Vt) \\ m\ddot{y} &= eA \cos \kappa(x+Vt) + eA \frac{\dot{x}}{V} \cos \kappa(x+Vt) \\ m\ddot{z} &= 0. \end{aligned} \right\} \quad \dots \quad (2)$$



Put  $x + Vt = \xi$ , so that  $\dot{\xi} = \dot{x} + V$ ,  $\ddot{\xi} = \ddot{x}$ , and the equations become

$$\begin{cases} m\ddot{\xi} = -eA \frac{\dot{y}}{V} \cos \kappa \xi, \\ m\ddot{y} = eA \frac{\dot{\xi}}{V} \cos \kappa \xi, \end{cases}$$

of which obvious first integrals are

$$\begin{aligned} \dot{\xi}^2 + \dot{y}^2 &= u^2 \\ \dot{y} &= \frac{eA}{\kappa m V} \sin \kappa \xi + v, \end{aligned}$$

where  $u, v$  are new constant velocities. Eliminating  $\dot{y}$ , we obtain as the equation for  $\xi$ ,

$$\dot{\xi}^2 = u^2 - \left( v + \frac{eA}{\kappa m V} \sin \kappa \xi \right)^2,$$

or putting  $\theta = \tan \frac{1}{2} \kappa \xi$ ,

$$\frac{1}{\kappa^2} \dot{\theta}^2 = (u^2 - v^2)(1 + \theta^2) - \frac{4eA}{\kappa m V} v \theta (1 + \theta^2) + \frac{4e^2 A^2}{\kappa^2 m^2 V^2} \theta^2.$$

From this the value of  $\theta$  may be written down as an elliptic function of the time, but the solution is of greater complexity than is either convenient or necessary for our purpose.

The same reason which enabled us to limit ourselves to low temperatures also permits us to consider only the case in which the light is of feeble intensity—we may neglect squares of  $A$ . The equation now becomes identical with

$$\frac{4}{\kappa^2} \dot{\theta}^2 = (u^2 - v^2) \left[ 1 + \theta^2 - \frac{2eAv\theta}{(u^2 - v^2)\kappa m V} \right]^2,$$

or, if  $u^2 - v^2 = w^2$ , so that  $w$  is another constant velocity,

$$\frac{2}{\kappa} \dot{\theta} = w \left( 1 - \frac{2eAv}{w^2 \kappa m V} \theta + \theta^2 \right),$$

leading to the integral

$$\tan \frac{1}{2} \kappa \xi = \tan \frac{1}{2} \kappa w t + \frac{eAv}{w^2 \kappa m V},$$

in which we avoid adding a constant of integration if we  
*Phil. Mag.* S. 6. Vol. 27. No. 157. Jan. 1914. C

suppose the origin from which  $t$  is measured to remain indefinite. We readily obtain

$$\xi = wt + \frac{eAv}{w^2\kappa^2mV} \cos \kappa wt,$$

and hence

$$\left. \begin{aligned} x &= (w - V)t + \frac{eAv}{w^2\kappa^2mV} \cos \kappa wt \\ y &= vt - \frac{eA}{w\kappa^2mV} \cos \kappa wt \\ z &= w_0t \end{aligned} \right\}, \quad \dots \quad (3)$$

in which, strictly speaking, constants of integration must be added to  $x$ ,  $y$ ,  $z$ , and  $t$ .

It now appears that the motion of the electron may be regarded as compounded of

- (i.) a uniform velocity of translation,  $u_0$ ,  $v_0$ ,  $w_0$ ;
- (ii.) oscillations parallel to the axes of  $x$  and  $y$ , each of a purely harmonic nature, and of frequency  $\kappa w$ .

Since  $w = u_0 + V$ , the result is such as might have been anticipated from the Doppler theory. but it is not easy to give a rigorous proof without a detailed examination of the equations of motion.

3. The electron will, according to the classical dynamics, absorb light of frequency  $\kappa V$ ; it will emit light whose frequency will vary according to the direction of emission, the frequency in any direction being obtained by modifying the frequency of oscillation  $\kappa w$  in accordance with Doppler's principle.

Let polar coordinates  $r$ ,  $\theta$ ,  $\psi$  be taken, the axis of  $x$  being taken for  $\theta = 0$ , and the plane of  $xy$  for  $\psi = 0$ . The velocity of the electron has a component in the direction  $\theta$ ,  $\psi$  equal to

$$u_0 \cos \theta + v_0 \sin \theta \cos \psi + w_0 \sin \theta \sin \psi,$$

so that the frequency, say  $q$ , of the radiation emitted in this direction will be given by

$$q = \frac{\kappa w}{V} (V - u_0 \cos \theta - v_0 \sin \theta \cos \psi - w_0 \sin \theta \sin \psi). \quad (4)$$

Let us assume the distribution in different directions of the radiation emitted by the electron to be

$$I(\theta, \psi) \sin \theta \, d\theta \, d\psi.$$

Let  $c_0^2$  stand for  $u_0^2 + v_0^2 + w_0^2$ , and let the mean-square velocity of the electron, averaged over a great length of time, be  $c^2$ . Let the proportion of the whole time during which the velocity components lie within a small range  $du_0 dv_0 dw_0$ , be

$$A f\left(\frac{u_0^2 + v_0^2 + w_0^2}{c^2}\right) du_0 dv_0 dw_0.$$

Then the total radiant energy emitted by the electron per unit time will, on the average, be

$$\iiint A f\left(\frac{u_0^2 + v_0^2 + w_0^2}{c^2}\right) I(\theta, \psi) \sin \theta d\theta d\psi du_0 dv_0 dw_0, \quad (5)$$

the integration being over all values of  $\theta$ ,  $\psi$ ,  $u_0$ ,  $v_0$ , and  $w_0$ , and the frequency of any element of the light being given by equation (4).

To analyse this radiation according to frequency, we may change the variables from  $u_0$ ,  $v_0$ ,  $w_0$ ,  $\theta$ , and  $\psi$  to  $u_0$ ,  $w_0$ ,  $\theta$ ,  $\psi$ , and  $q$ . Writing  $q_0$  for  $\kappa V$ , the frequency of the incident light, we have

$$v_0 = \frac{1}{\sin \theta \cos \psi} \left\{ V - u_0 \cos \theta - w_0 \sin \theta \sin \psi - \frac{q}{q_0} \frac{V^2}{V + u_0} \right\}$$

$$\frac{\partial v_0}{\partial q} = - \frac{1}{q_0} \frac{V^2}{(V + u_0) \sin \theta \cos \psi},$$

whence integral (5) may be written in the form

$$A \int dq \iiint f \left\{ \frac{1}{c^2} (u_0^2 + w_0^2) + \frac{1}{c^2} \operatorname{cosec}^2 \theta \sec^2 \psi \right. \\ \left. \times \left( V - u_0 \cos \theta - w_0 \sin \theta \sin \psi - \frac{q V^2}{q_0 (V + u_0)} \right)^2 \right\} \\ \times I(\theta, \psi) \frac{1}{q_0} \frac{V^2}{(V + u_0)} \operatorname{cosec} \theta \sec \psi d\theta d\psi du_0 dw_0, \quad (6)$$

of which the form after integration is

$$\int \frac{1}{q_0} \Phi\left(\frac{q}{q_0}, c^2\right) dq. \quad (7)$$

4. Suppose the electron is in a region of space in which the law of partition of radiant energy is  $\phi(q_0) dq_0$ , the energy being distributed at random as regards direction. Suppose that unit energy of frequency  $q$  is, as the result of interaction with the electron, after unit time replaced by energy  $\theta(q_0)$  of the original frequency  $q_0$ , and a spectrum  $\int F(q_0, q) dq$  of



scattered energy. By the result of § 3,  $F(q_0, q)$  must be of the form

$$F(q_0, q) = \frac{1}{q_0} \Phi\left(\frac{q}{q_0}, c^2\right), \quad . \quad . \quad . \quad (8)$$

and so, by the conservation of energy,

$$1 - \theta(q_0) = \int_0^\infty F(q_0, q) dq = \int_0^\infty \Phi\left(\frac{q}{q_0}, c^2\right) \frac{dq}{q_0}.$$

On integration this last is a function of  $c^2$  only, so that  $\theta(q_0)$  does not depend on  $q_0$ , and may be replaced by  $\theta$ .

The law of partition of the whole energy after unit time is

$$\int dq_0 \theta \phi(q_0) + \int dq \int_0^\infty \phi(q_0) F(q_0, q) dq,$$

or arranged according to frequency  $q$ ,

$$\int dq \left[ \theta \phi(q) + \int_0^\infty \phi(q_0) F(q_0, q) dq_0 \right]. \quad . \quad . \quad (9)$$

If the radiation in the space is to be in temperature equilibrium with the electron, the partition of energy must be unaltered by the interaction between the electron and the radiation. The final partition of energy (9) must accordingly be identical with the initial partition of energy  $\int dq \phi(q)$ . Thus we must have

$$\theta \phi(q) + \int_0^\infty \phi(q_0) F(q_0, q) dq_0 = \phi(q),$$

or by equation (8)

$$\phi(q) [1 - \theta] = \int_0^\infty \phi(q_0) \Phi\left(\frac{q}{q_0}, c^2\right) \frac{dq_0}{q_0}, \quad . \quad . \quad (10)$$

and the partition of energy required,  $\phi(q)$ , is the solution of this integral equation.

The equation may be written

$$\int_0^\infty \frac{\phi(q_0)}{\phi(q)} \left(\frac{q}{q_0}\right) \Phi\left(\frac{q}{q_0}, c^2\right) d\left(\frac{q_0}{q}\right) = 1 - \theta,$$

or, if  $q_0 = uq$ ,

$$\int_{u=0}^{u=\infty} \frac{\phi(uq)}{\phi(q)} \Phi\left(\frac{1}{u}, c^2\right) \frac{du}{u} = 1 - \theta,$$

so that the ratio of  $\phi(uq)$  to  $\phi(q)$  must be independent of  $q$ .

The solution is easily found to be

$$\phi(q) = Cq^n, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

in which  $C$  and  $n$  are constants.

5. It is at once obvious that this form cannot include Planck's formula. Thus we have seen that there is nothing (so far as the evidence of the radiation formula goes) which is untrue in the ordinarily assumed laws for free æther, or in the ordinarily assumed thermodynamical laws, but it now appears that there must be something untrue in the equations which have been used as the basis of the analysis of §§ 2, 3. It is somewhere in these equations that the break between the classical dynamics and the true dynamics must occur.

6. Any attempt to localize still more definitely the exact point of failure of the classical equations must of necessity involve a detailed discussion of the equations of which we have made use.

In equations (1) it may first be noticed that the terms in square brackets, representing *emission*, have not been used at all—equations (1) were immediately replaced by equations (2) because it was found that the terms in equation (1) in square brackets were negligible for the particular crucial problem we were testing. Nothing, then, is to be gained by discussing whether the terms in square brackets are accurate or inaccurate. But two assumptions have been made about the emission—first that the emission terms in equation (1) may be neglected for the special problem under consideration, and, second, (in § 3), that a simple-harmonic motion of a free electron results in an emission of light of the same frequency. Both these assumptions must of course be regarded as being under suspicion.

For the rest, we have assumed the truth of equations (2), which are simply the equations of action of electric and magnetic forces on an electron as a whole. Experiments on electrons moving in electric and magnetic fields (*e. g.* determinations of  $e/m$ ) seem to indicate that these equations are at least true for steady fields, and, so long as we assume that the action on an electron at any instant depends solely on the field at that instant, it is hard to see how the equations can fail to be true for varying fields also.

One other assumption has been implied: namely, that a single free electron in a field of radiant energy is a possible dynamical system. It may be that the simplest system which can be considered is not a single free electron but a tube of force with an electron at one end and a positive charge at the other.

7. Apart from these speculations, the definite result seems to emerge, that the departure from the classical mechanics is to be looked for in the fundamental equations of æther and electricity. Nothing so complicated as the structure of matter appears to be involved. It is not a question of modifying our ideas (in so far as we have ideas) on the build of atoms or molecules: we are called on to revolutionize views which have long been regarded as well-established on the nature or meaning of electricity, æther, or radiation.

### III. *On Canonical Relations in General Dynamics.*

*By* Professor A. GRAY, F.R.S.\*

1. **I**N a paper on General Dynamics (Proc. R. S. E., Feb. 19, 1912) I have derived Hamilton's principal function  $S$ , and the parallel function  $S'$  [§ 5, (1) below], with the corresponding partial differential equations, by a direct process not involving the calculus of variations. Hamilton's Principle and the Principle of Least Action may, as exemplified below, be deduced from the functions  $S$ ,  $S'$ , and it will be seen that the use of the two functions facilitates the proof and discussion of various other theorems.

It may be recalled that the canonical equations of a system, unacted on by friction, and defined by  $k$  coordinates,  $q_1, q_2, \dots, q_k$ , that is the  $2k$  equations of the type

$$\frac{dp}{dt} = -\frac{\partial H}{\partial q}, \quad \frac{dq}{dt} = \frac{\partial H}{\partial p} \quad . \quad . \quad . \quad . \quad (1)$$

can, as Jacobi proved, be replaced by finite equations, if the complete integral of the Hamiltonian differential equation

$$\frac{\partial S}{\partial t} + H\left(\frac{\partial S}{\partial q_1}, \frac{\partial S}{\partial q_2}, \dots, \frac{\partial S}{\partial q_k}, q_1, q_2, \dots, q_k, t\right) = 0 \quad . \quad (2)$$

can be found.

Here

$$H = \Sigma(p\dot{q}) - T + V, \quad . \quad . \quad . \quad . \quad (3)$$

and  $p(=\partial T/\partial \dot{q})$  is derived from  $T$ , the kinetic energy expressed as a function of the  $q$ 's,  $\dot{q}$ 's, and, it may be, of  $t$ . Since the solution of a dynamical problem consists in the expression of the values of the coordinates, the velocities (the  $\dot{q}$ 's) [or the momenta (the  $p$ 's)] in terms of  $t$  and initial

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values  $a_1, a_2, \dots, a_k, b_1, b_2, \dots, b_k$ , say, of the  $q$ 's and  $p$ 's,  $H$  can be expressed for time  $t$  in terms of the  $a$ 's, the  $b$ 's,  $t$  and  $\tau$ , or, if we please, in terms of the  $p$ 's, the  $q$ 's, and  $t$ . It is desirable for clearness to state explicitly in all dynamical relations which are obtained what are the variables in terms of which the different quantities are supposed to be expressed.

2. It is not unusual to assume tacitly that the reciprocal relations discussed in §§ 6....11 below, when established, *in form*, as consequences of the fact that two successive partial differentiations of a certain function of the initial and final coordinates (or momenta) are commutative, hold also when the quantities of which derivatives are taken are quite differently expressed. For example from the relation

$$\frac{\partial S}{\partial a_i} = -b_i \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $S$  is a function of the  $q$ 's and the  $a$ 's, and therefore so also is  $b_i$ , we get, since  $\partial S / \partial q = p$ ,

$$\frac{\partial p}{\partial a_i} = -\frac{\partial b_i}{\partial q} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Now the dynamical relation which is of real practical importance is one of exactly the same *form*, which holds when  $p$  is expressed as a function of the initial coordinates and momenta and  $t$ , while  $b_i$  is expressed as a function of the *final* coordinates and momenta and  $t$ . It is one of the objects of the present paper to supply the necessary proof of the permanence of form here exemplified by a particular case of a very general property of canonical relations.

3. The determination of the complete integral of (2) § 1, consists in finding  $S$  as a function of  $q_1, q_2, \dots, q_k, t$ , and  $k$  coordinates  $\alpha_1, \alpha_2, \dots, \alpha_k$  (which may be the  $k$  initial coordinates, or any  $k$  independent functions of these) and  $\tau$ , the initial value of the time, which, if it is convenient to do so, may be taken as zero. The finite equations are then

$$\frac{\partial S}{\partial \alpha_1} = \beta_1, \dots, \frac{\partial S}{\partial \alpha_k} = \beta_k \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If  $a_1, a_2, \dots, a_k$ , the initial coordinates are used, the finite equations become, as is well known, and will be shown in what follows,

$$\frac{\partial S}{\partial a_1} = -b_1, \dots, \frac{\partial S}{\partial a_k} = -b_k \quad . \quad . \quad . \quad (2)$$

It is in general to be understood that the coordinates, the  $q$ 's, at time  $t$ , are independent functions of the initial coordinates and momenta. That is, varying these coordinates, subject, say, to the condition that only the  $b$ 's are changed, we get  $k$  equations of the form

$$\delta q_i = \sum_{j=1}^{j=k} \frac{\partial q_i}{\partial b_j} \delta b_j. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The condition for the independence of  $\delta q_1, \delta q_2, \dots, \delta q_k$  is the non-evanescence of the determinant

$$\Sigma \pm \frac{\partial q_1}{\partial b_1} \frac{\partial q_2}{\partial b_2} \dots \frac{\partial q_k}{\partial b_k}.$$

Since  $q_1, q_2, \dots, q_k$  are independent the speeds  $\dot{q}_1, \dot{q}_2, \dots, \dot{q}_k$  are also independent; so also are the momenta for time  $t$ , namely,

$$p_1 = \frac{\partial T}{\partial \dot{q}_1}, \quad \dots, \quad p_k = \frac{\partial T}{\partial \dot{q}_k}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

as can easily be proved. Now by the canonical equations

$$\dot{q}_1 = \frac{\partial H}{\partial p_1}, \quad \dot{q}_2 = \frac{\partial H}{\partial p_2}, \quad \dots, \quad \dot{q}_k = \frac{\partial H}{\partial p_k}, \quad . \quad . \quad (5)$$

we have  $k$  equations of the form

$$\delta \dot{q}_i = \sum_{j=1}^{j=k} \frac{\partial^2 H}{\partial p_j \partial p_i} \delta p_j, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and the determinant

$$\Sigma \pm \frac{\partial^2 H}{\partial p_1 \partial p_1} \frac{\partial^2 H}{\partial p_2 \partial p_2} \dots \frac{\partial^2 H}{\partial p_k \partial p_k}$$

does not vanish.

It is to be understood in what follows, except where the contrary is specified, that these conditions of independence are fulfilled.

4. Reserving then  $a_1, a_2, \dots, a_k$  to denote the initial coordinates, we shall denote the constants in  $S$  by  $\alpha_1, \alpha_2, \dots, \alpha_k$ , and prove that the substitution of any other set of constants  $c_1, c_1, \dots, c_k$ , say, connected with the  $\alpha$ 's by  $k$  independent equations of the form

$$\begin{aligned} \alpha_1 &= \phi_1(t, q_1, \dots, q_k, c_1, \dots, c_k), \\ \alpha_2 &= \phi_2(t, q_1, \dots, q_k, c_1, \dots, c_k), \text{ etc.} \quad . \quad (1) \end{aligned}$$

does not cause any change in the values of the  $p$ 's (initial and final) provided the value of the integral

$$S_1 = \int_{\tau}^t \{ \Sigma(p\dot{q}) - H \} dt, \quad . \quad . \quad . \quad . \quad (2)$$

is taken as the complete value of the principal function. [Of course it will be understood that the substitution of the values of  $q_1, q_2, \dots, q_k$  in terms of  $t$  and the  $2k$  constants, the  $a$ 's and the  $b$ 's, leads to equations of the form

$$\alpha_1 = \chi_1(a_1, \dots, a_k, b_1, \dots, b_k), \alpha_2 = \chi_2(a_1, \dots, a_k, b_1, \dots, b_k), \dots]$$

The use of this form of the principal function amounts to the introduction of an additive constant as in the equation

$$S_1 = S(t, q_1, \dots, q_k, \alpha_1, \dots, \alpha_k) - S_0, \quad . \quad . \quad . \quad (3)$$

where  $S_0$  is what  $S$  becomes when  $\tau$  is substituted for  $t$ , and the initial coordinates, the  $a$ 's, for the  $q$ 's. Now since  $\partial S / \partial \alpha$  does not change with  $t$ , (3) gives the relations

$$\frac{\partial(S - S_0)}{\partial \alpha_1} = 0, \quad \frac{\partial(S - S_0)}{\partial \alpha_2} = 0, \quad \dots, \quad \frac{\partial(S - S_0)}{\partial \alpha_k} = 0. \quad (4)$$

Let the  $\alpha$ 's in  $S_1$  be replaced by their values as given by (1), thus introducing the  $c$ 's. Denoting the value of  $\partial S_1 / \partial q$  taken after this substitution by  $(\partial S_1 / \partial q)$ , we obtain

$$\left( \frac{\partial S_1}{\partial q} \right) = \frac{\partial S}{\partial q} + \frac{\partial S_1}{\partial \alpha_1} \frac{\partial \alpha_1}{\partial q} + \frac{\partial S_1}{\partial \alpha_2} \frac{\partial \alpha_2}{\partial q} + \dots + \frac{\partial S_1}{\partial \alpha_k} \frac{\partial \alpha_k}{\partial q} = \frac{\partial S}{\partial q}, \quad (5)$$

since by (4)

$$\partial S_1 / \partial \alpha_1 = \partial S_1 / \partial \alpha_2 = \dots = \partial S_1 / \partial \alpha_k = 0.$$

Thus the values of the  $p$ 's are not altered by the change to new constants.

The coordinate  $q$  appears explicitly only in  $S$ , and the corresponding initial coordinate  $a$  only in  $S$ . As

$$\partial S_1 / \partial \alpha_1 = \partial S_1 / \partial \alpha_2 = \dots = 0,$$

the appearance of the  $a$ 's in the  $\alpha$ 's may be neglected; and so we have

$$\frac{\partial S}{\partial q} = p, \quad \frac{\partial S_0}{\partial a} = b, \quad . \quad . \quad . \quad . \quad (6)$$

for the corresponding momenta at times  $t$  and  $\tau$ .

If we suppose the time to flow back from  $t$  to  $\tau$  and the momenta to be reversed for every value of  $t$  without change



in amount, the initial and final configurations become interchanged, and the sequence of configurations is the former sequence taken in the reverse order. The momentum corresponding to the coordinate  $a$  is then  $\partial S/\partial a$ ; and so in the forward motion we have

$$\frac{\partial S}{\partial a} = -b \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If the constants are the initial coordinates (or as we shall see the initial momenta)  $S_0$  may be dispensed with. But then the values of  $\partial S/\partial a$  obtained by putting  $t=\tau$ , and  $(q_1, q_2, \dots) = (a_1, a_2, \dots)$  do not fix the values of the  $b$ 's; on the contrary the values of the  $b$ 's, otherwise assigned, fix the values of the derivatives. The values of the  $a$ 's, or  $c$ 's, must be so chosen as to make the derivatives,  $\partial S_0/\partial a$ , have the proper assigned values.

Considerations similar to these apply to the function  $S'$  and the constants used in its expression.

It is important to notice that by what precedes the  $k$  constants used may be the initial momenta.  $S$  is then expressed as a function of the initial momenta and the final coordinates. But  $S'$  [§ 5, (1)] may be expressed in terms of the  $p$ 's and the mutual coordinates, that is of the initial coordinates and the final momenta. Thus in a reversed motion when the time flows back from  $t$  to  $\tau$  the function  $S$  for the forward motion becomes the function  $S'$  for the backward motion, and the reciprocal nature of the functions is further emphasized.

Now in the forward motion  $\partial S'/\partial p = q$ . Hence in the backward motion we have  $\partial S'/\partial b_i = -a_i$ ; or by the remark just made

$$\frac{\partial S}{\partial b_i} = a_i \quad . \quad . \quad . \quad . \quad . \quad (8)$$

when  $S$  is expressed in terms of the  $q$ 's and the  $b$ 's.

5. The functions defined by the equations

$$S = \int_{\tau}^t \{ \Sigma(p\dot{q}) - H \} dt, \quad S' = \int_{\tau}^t \{ \Sigma(\dot{p}q) + H \} dt \quad . \quad (1)$$

when  $S$  is determined as a function of the  $q$ 's and  $k$  constants, and  $S'$  as a function of the  $p$ 's and  $k$  constants, with

$$\frac{\partial S}{\partial q} = p, \quad \frac{\partial S'}{\partial p} = q, \quad . \quad . \quad . \quad . \quad (2)$$

obviously satisfy the partial differential equations

$$\frac{\partial S}{\partial t} + H = 0, \quad \frac{\partial S'}{\partial t} - H = 0. \quad . \quad . \quad . \quad (3)$$

These lead at once to the equations

$$\frac{\partial p}{\partial t} = -\frac{\partial H}{\partial q}, \quad \frac{\partial q}{\partial t} = \frac{\partial H}{\partial p}, \quad . \quad . \quad . \quad . \quad (4)$$

which are the same in form as the canonical equations, except that on the left the differentiation with respect to  $t$  is partial instead of total. In the first  $p$  is  $\partial S/\partial q$ , and is therefore a function of  $t$ , the  $q$ 's, and  $k$  constants, and so also is  $H$ ; in the second  $q$  is  $\partial S'/\partial p$ , and is, with  $H$ , a function of  $t$ , the  $p$ 's, and  $k$  constants. There are of course  $k$  pairs of these equations.

If in (4) the  $q$ 's and the  $p$ 's are replaced by their values in terms of the  $2k$  constants and  $t$ , the equations hold without alteration of form, for then they are precisely the canonical equations, since partial differentiation of  $q$  and  $p$  with respect to  $t$  then means the same thing as total differentiation. In other words, the canonical equations assert that partial differentiation of  $p$  (or of  $q$ ), with respect to  $t$ , when the quantity differentiated is expressed in terms of  $t$  and the initial coordinates and momenta, is the same thing as partial differentiation with respect to  $q$  of  $\partial S/\partial t$  (or with respect to  $p$  of  $\partial S'/\partial t$ ) when the subject of differentiation is expressed in terms of  $t$  and the *final* coordinates and momenta.

6. This remarkable connexion between the initial and the final coordinates and momenta holds for differentiation with respect to other variables than  $t$ , *e.g.* we can choose any of the  $a$ 's or the  $b$ 's. There are in fact a set of canonical equations for every variable we thus select.

For example, if we differentiate with respect to  $q$  the equation [(7), § 4, above]

$$\frac{\partial S}{\partial a_i} = -b_i, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where both sides are regarded as functions of the  $q$ 's, the  $a$ 's, and  $t$ , we get

$$\frac{\partial p}{\partial a_i} = \frac{\partial^2 S}{\partial q \partial a_i} = -\frac{\partial b_i}{\partial q}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

an equation which is comparable with

$$\frac{\partial p}{\partial t} = -\frac{\partial H}{\partial q}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and which retains its form when we express  $p$  as a function of the initial coordinates and momenta and  $t$ , while  $b_i$  is expressed as a function of the final coordinates and momenta and  $t$ . Thus, denoting differentiation, carried out on these

suppositions as to the mode in which  $p$  and  $b_i$  are expressed, by enclosing the derivatives in brackets, we get

$$\left(\frac{\partial p}{\partial a_i}\right) = -\left(\frac{\partial b_i}{\partial q}\right) \dots \dots \dots (4)$$

Similarly from (8), § 4, we get the relation

$$\frac{\partial p}{\partial b_i} = \frac{\partial^2 S}{\partial b_i \partial q} = \frac{\partial a_i}{\partial q}, \dots \dots \dots (5)$$

(where  $S$  is supposed to be expressed in terms of the  $q$ 's, the  $b$ 's, and  $t$ , and  $p$  and  $a_i$  are expressed in like manner) which retains its form when  $p$  is expressed in terms of the initial coordinates and momenta and  $t$ , and  $a_i$  is expressed in terms of the *final* coordinates and momenta and  $t$ , so that

$$\left(\frac{\partial p}{\partial b_i}\right) = \left(\frac{\partial a_i}{\partial q}\right) \dots \dots \dots (6)$$

Two other reciprocal relations are derived in the same way from the function  $S'$  and also retain their form when a similar change of expression is effected for the quantities differentiated. These are

$$\left(\frac{\partial q}{\partial b_i}\right) = -\left(\frac{\partial a_i}{\partial p}\right), \quad \left(\frac{\partial q}{\partial a_i}\right) = \left(\frac{\partial b_i}{\partial p}\right) \dots \dots \dots (7)$$

7. The parallelism of these equations with the canonical equations is made clearer if we replace  $t$  by a symbol  $u$  which we regard as a coordinate in the generalised sense, and associate with a momentum  $v$ . Then if we put  $H' = H + v$ , and write the additional canonical equations,

$$\frac{du}{dt} = \frac{\partial H'}{\partial v} (=1), \quad \frac{dv}{dt} = -\frac{\partial H'}{\partial u}, \dots \dots \dots (1)$$

we obtain, since  $\partial H'/\partial u = \partial H/\partial t = \partial H/\partial t$  (by the canonical equations),

$$H + v = \text{const.} \dots \dots \dots (2)$$

Thus the partial differential equation becomes, since  $\partial S/\partial u = v$ ,

$$\frac{\partial S}{\partial u} + H = \text{const.}, \dots \dots \dots (3)$$

which takes its place with others, such as

$$\frac{\partial S}{\partial a_i} + b_i = 0, \dots \dots \dots (4)$$

as the foundation of the various canonical relations.

The device of regarding the time as a coordinate is useful in many respects as we shall see later. It has been employed by Poincaré, Minkowski, and others in various applications.

8. The relations (4), (6), (7) of § 6 appear to have been first published by Donkin (Phil. Trans. 1855), but they are contained in one of five undated papers by Jacobi (*Nachgelassene Abhandlungen*) appended by Clebsch to his edition of the *Vorlesungen über Dynamik*, published at Berlin in 1866. Jacobi died in 1851. All possible relations of this kind, including the usual canonical equations, are involved in an extended form of a variational theorem due to Lagrange, which is most easily and directly established by means of the function  $S$ , and constitutes a fundamental relation between initial and final coordinates. As stated in the former paper, equations (4), (6) and (7) of § 6 were, in part at least, rediscovered and interpreted by v. Helmholtz (Crelle, 1866), and illustrations were given by Lamb (Proc. Lond. Math. Soc. 1866), who also derived v. Helmholtz's results from Lagrange's theorem.

9. Assuming the canonical equations we can now derive two theorems by means of which (4), (6) and (7) of § 5 can be inferred. The proof by inference (the idea of which becomes clearer when  $t$  is regarded as a coordinate) may be justified in various ways, *e. g.* by a process due to Jacobi (*Nachg. Abhandl., Vorlesungen*, p. 395). In the canonical equations  $H$ , as has been stated, is a function of  $(t, q, p)^*$ , and the constants do not appear. The transformation of  $H$  from the form in which it is used in (4) of § 4 is by substitution from the equations

$$a_i = \zeta_i(q_1, \dots, q_k, p_1, \dots, p_k, t), \quad \dots \quad (1)$$

or from

$$b_i = \theta_i(q_1, \dots, q_k, p_1, \dots, p_k, t), \quad \dots \quad (2)$$

[according as the variables transformed are  $(t, q, a)$  or  $(t, q, b)$ ], which give the initial coordinates and momenta in terms of the final values of these quantities and the time.

Now from the equations

$$\frac{dp}{dt} = -\frac{\partial H}{\partial q}, \quad \frac{\partial p}{\partial t} = -\frac{\partial H}{\partial t}, \quad \dots \quad (3)$$

where of course  $H$  is supposed expressed in the two different

\* Here, and in what follows,  $(t, q, p)$  signifies the variables  $t, q_1, q_2, \dots, q_k, p_1, p_2, \dots, p_k$ . Similar abbreviations are used in other cases.



ways specified above, we obtain

$$\frac{\partial p}{\partial q_1} \dot{q}_1 + \frac{\partial p}{\partial q_2} \dot{q}_2 + \dots + \frac{\partial p}{\partial q_k} \dot{q}_k = - \left( \frac{\partial H}{\partial a_1} \frac{\partial a_1}{\partial q} + \frac{\partial H}{\partial a_2} \frac{\partial a_2}{\partial q} + \dots + \frac{\partial H}{\partial a_k} \frac{\partial a_k}{\partial q} \right), \quad (4)$$

which may be written in the form

$$\frac{\partial^2 S}{\partial q_1 \partial q} \dot{q}_1 + \dots + \frac{\partial^2 S}{\partial q_k \partial q} \dot{q}_k = \frac{\partial^2 S}{\partial a_1 \partial t} \frac{\partial a_1}{\partial q} + \dots + \frac{\partial^2 S}{\partial a_k \partial t} \frac{\partial a_k}{\partial q}. \quad (5)$$

Similarly from the equations

$$\frac{dq}{dt} = \frac{\partial H}{\partial p}, \quad \frac{\partial q}{\partial t} = \frac{\partial H}{\partial p}, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

we obtain

$$\frac{\partial^2 S'}{\partial p_1 \partial p} \dot{p}_1 + \dots + \frac{\partial^2 S'}{\partial p_k \partial p} \dot{p}_k = \frac{\partial^2 S'}{\partial b_1 \partial t} \frac{\partial b_1}{\partial p} + \dots + \frac{\partial^2 S'}{\partial b_k \partial t} \frac{\partial b_k}{\partial p}. \quad (7)$$

Instead of differentiating with respect to  $t$  as in (3) we may do so with respect to any of the constants. In the canonical equations  $H$  is  $-\partial S/\partial t$  in one case and  $\partial S'/\partial t$  in the other, and is expressed in each case as a function of  $(t, p, q)$ . Now consider in the same way  $-\partial S/\partial a_i$ , or  $\partial S'/\partial b_i$ , as a function of  $(t, p, q)$ . The former is  $b_i$ , the latter is  $-a_i$ . This suggests putting in (3) above  $b_i$  for  $H$ , and taking  $\dot{q}_1, \dot{q}_2, \dots, \dot{q}_k$  on the left as standing for  $\partial q_1/\partial a_i, \partial q_2/\partial a_i, \dots, \partial q_k/\partial a_i$ , so that we obtain instead of (4)

$$\frac{\partial p}{\partial q_1} \frac{\partial q_1}{\partial a_i} + \dots + \frac{\partial p}{\partial q_k} \frac{\partial q_k}{\partial a_i} = - \left( \frac{\partial b_i}{\partial a_1} \frac{\partial a_1}{\partial q} + \dots + \frac{\partial b_i}{\partial a_k} \frac{\partial a_k}{\partial q} \right). \quad (8)$$

Adding to this the equation (2) § 5, namely,

$$\frac{\partial p}{\partial a_i} = - \frac{\partial b_i}{\partial q}, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

we obtain

$$\left( \frac{\partial p}{\partial a_i} \right) = - \left( \frac{\partial b_i}{\partial q} \right). \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Similarly by means of the second function  $S'$  we deduce the relation

$$\left( \frac{\partial q}{\partial b_i} \right) = - \left( \frac{\partial a_i}{\partial p} \right); \quad . \quad . \quad . \quad . \quad . \quad (11)$$

and the remaining two relations stated in § 6 above can be found in like manner.

10. The passage from  $\partial q/\partial t = \partial H/\partial p$ ,  $\partial p/\partial t = -\partial H/\partial q$ , (with  $p = \partial S/\partial q$ ) where  $H$  is a function of the  $q$ 's,  $t$ , and  $k$  constants, to  $dq/dt = \partial H/\partial p$ ,  $dp/dt = -\partial H/\partial q$ , where  $H$  is a function of  $(p, q, t)$ , and the establishment of the four relations given above, were effected by Jacobi (*Vorlesungen*, p. 395) by a direct process which seems to have escaped the notice of most of those who have written on the canonical equations. With some modifications it is shortly as follows. The substitution of the values of the  $a$ 's in  $\partial S/\partial q$  in terms of  $(p, q, t)$  must lead to the identity  $p = p$ . Hence differentiating on the supposition that this substitution has been effected, we get

$$\frac{\partial p_j}{\partial q} + \frac{\partial p_j}{\partial a_1} \frac{\partial a_1}{\partial q} + \dots + \frac{\partial p_j}{\partial a_k} \frac{\partial a_k}{\partial q} = 0. \quad . \quad . \quad (1)$$

There are  $k$  such equations. Multiplying them in order by  $\partial q_1/\partial a_i$ ,  $\partial q_2/\partial a_i$ , ..., and adding, we get

$$\frac{\partial p_1}{\partial q} \frac{\partial q_1}{\partial a_i} + \frac{\partial p_2}{\partial q} \frac{\partial q_2}{\partial a_i} + \dots + \frac{\partial p_k}{\partial q} \frac{\partial q_k}{\partial a_i} + R = 0, \quad . \quad (2)$$

where  $R$  is the sum of all the terms except those which are the first terms on the left of the equations.

But we have also

$$\frac{\partial S}{\partial a_i} = -b_i, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and it is clear that if we substitute in  $\partial S/\partial a_i$  the values of the coordinates in terms of the  $2k$  constants and  $t$ , this equation will reduce to the identity  $b_i = b_i$ . We have therefore  $k$  equations of the form

$$-\left(\frac{\partial b_j}{\partial a_i}\right) = \frac{\partial^2 S}{\partial a_i \partial a_j} + \frac{\partial^2 S}{\partial q_1 \partial a_j} \frac{\partial q_1}{\partial a_i} + \dots + \frac{\partial^2 S}{\partial q_k \partial a_j} \frac{\partial q_k}{\partial a_i} = 0. \quad (4)$$

Multiplying these in order by  $\partial a_1/\partial q$ ,  $\partial a_2/\partial q$ , ..., (where the  $a$ 's are regarded as functions of the variables  $(p, q, t)$ ), and adding the set of equations together, we obtain

$$\frac{\partial^2 S}{\partial a_1 \partial a_i} \frac{\partial a_1}{\partial q} + \frac{\partial^2 S}{\partial a_2 \partial a_i} \frac{\partial a_2}{\partial q} + \dots + \frac{\partial^2 S}{\partial a_k \partial a_i} \frac{\partial a_k}{\partial q} + R = 0, \quad (5)$$

where  $R$  has the same value as in (2).

Writing now  $\partial p/\partial q_1$ ,  $\partial p/\partial q_2$ , ..., instead of  $\partial p_1/\partial q$ ,  $\partial p_2/\partial q$ , ..., in (2), adding on the left of that equation  $\partial p/\partial a_i$ , and on the left of (5) the equal quantity  $\partial^2 S/\partial q \partial a_i$ , we get

$$\left(\frac{\partial p}{\partial a_i}\right) = -\left(\frac{\partial b_i}{\partial q}\right). \quad . \quad . \quad . \quad . \quad . \quad (6)$$

[The other relations (6) and (7) of § 6 may be proved in the same manner.]

11. Starting from the relations

$$\frac{\partial p}{\partial t} = -\frac{\partial H}{\partial q}, \quad \frac{\partial q}{\partial t} = \frac{\partial H}{\partial p}, \quad . . . . . (1)$$

which follow at once from

$$\frac{\partial S}{\partial t} = -H, \quad . . . . . (2)$$

and using the variable  $t$  instead of  $a_i$  in equations corresponding to (2), (4), (5) of § 10, we pass to the canonical equations

$$\frac{dp}{dt} = -\frac{\partial H}{\partial q}, \quad \frac{dq}{dt} = \frac{\partial H}{\partial p}, \quad . . . . . (3)$$

in which the meanings of  $\partial H/\partial q$ ,  $\partial H/\partial p$  have been changed, as explained above.

12. In the light of the Hamiltonian function  $S$  we now consider the variation of the trajectory of a holonomous system. Since, § 4,  $S_1 (= S - S_0)$  involves only the initial and final coordinates, with  $t$  and  $\tau$ , it has the same value for any passage of the system from a given initial to a given final configuration without variation of the time of starting or the time of arrival. If we consider a possible succession of configurations we can derive another succession from it by the process of variation; but, as is now well understood, the derived succession may or may not, according to the condition imposed on the system, be itself a possible one.

Let the configuration at time  $t$  be defined by the coordinates  $q_1, q_2, \dots, q_k$ . Then it is possible to assign another set of coordinates,  $q_1 + \delta q_1, q_2 + \delta q_2, \dots, q_k + \delta q_k$ , for the same instant  $t$ , and if the system be holonomous, that is if  $q_1, q_2, \dots, q_k$  be the coordinates left independent after satisfaction of the (finite) kinematical relations,  $\delta q_1, \delta q_2, \dots, \delta q_k$  are any perfectly arbitrary small changes in the coordinates. In this case the succession of configurations given by the different values of  $t$  will be a possible one for the system, if  $\delta q_1, \delta q_2, \dots, \delta q_k$  are continuous functions of  $t$ , such that at every point of the locus of the sequence of positions (taken by the representative point  $P$  whose position in  $k$ -dimensional space is defined by  $q_1, q_2, \dots, q_k$ ) there is a definite derivative.

The system is still holonomous if the kinematical conditions involve  $t$  explicitly, provided these conditions are

expressed by finite equations. If the  $q$ 's be connected by non-integrable differential relations the system is not holonomous, and a sequence of configurations given by varied coordinates is not in general a succession that can be taken by the system. We shall call a holonomous system *quasi-conservative* if the generalised forces are the partial derivatives  $-\partial V/\partial q_1, \dots, -\partial V/\partial q_k$  of a function  $V$  of the  $q$ 's and  $t$ . If  $t$  does not appear in  $V$ , or in the kinematical conditions the system is truly conservative.

13. We now consider the principle of Hamilton and the analogous principle of Least Action for both quasi-conservative and truly conservative systems. The representative point  $P$  moves from  $P_0$  at time  $\tau$  to  $P$  at time  $t$  along a path in the  $k$ -dimensional space—along a *trajectory* in that space. if  $A_0$  be a locus of possible positions of  $P_0$  at time  $\tau$  a corresponding locus  $A$  will exist for each value of  $t$ . The corresponding loci will be of the same kind, for example both curves or both surfaces.

Now let the trajectory be varied from that joining two corresponding points  $C_0, C$  to a neighbouring trajectory joining two corresponding points  $D_0, D$ . If  $q_1, q_2, \dots, q_k$  be coordinates at time  $t$  and  $q_1 + \delta q_1, q_2 + \delta q_2, \dots, q_k + \delta q_k$  be coordinates of the corresponding point in the varied motion at the same instant, then since both paths of the representative point are possible, and the times of starting and arrival are the same for both, we have

$$\begin{aligned} \delta S_1 &= \Sigma \left( \frac{\partial S_1}{\partial q} \delta q \right) + \Sigma \left( \frac{\partial S_1}{\partial a} \delta a \right) \\ &= \Sigma (p \delta q) - \Sigma (b \delta a). \quad . \quad . \quad . \quad . \quad . \quad (1) \end{aligned}$$

If  $D_0$  coincide with  $C_0$  and  $D$  with  $C$  the value of  $\delta S$  for the interval  $t - \tau$  is zero. This is Hamilton's principle. Obviously it expresses the fact that

$$\delta \int_{\tau}^t L dt = 0; \quad . \quad . \quad . \quad . \quad . \quad (2)$$

for by definition

$$S_1 = \int_{\tau}^t L dt = \int_{\tau}^t \{ \Sigma (p \dot{q}) - H \} dt. \quad . \quad . \quad . \quad (3)$$

Thus  $S_1$  is stationary in value with respect to neighbouring paths of the representative point between the same terminal positions.



14. It may be noticed here that (1), § 13, gives at once Lagrange's variational equation referred to above. For let  $\delta, \delta'$  denote independent variations. We have

$$\delta \cdot \delta' q = \delta' \cdot \delta q, \quad \delta \cdot \delta' S_1 = \delta' \cdot \delta S_1, \quad . \quad . \quad (1)$$

and obtain

$$\left. \begin{aligned} \delta' \cdot \delta S_1 &= \Sigma (\delta' p \delta q - \delta' b \delta a + p \delta' \cdot \delta q - b \delta' \cdot \delta a) \\ \delta \cdot \delta' S_1 &= \Sigma (\delta p \delta' q - \delta b \delta' a + p \delta \cdot \delta' q - b \delta \cdot \delta' a) \end{aligned} \right\} \quad (2)$$

which give by subtraction Lagrange's equation

$$\Sigma (\delta' p \delta q - \delta p \delta' q) = \Sigma (\delta' b \delta a - \delta b \delta' a). \quad . \quad . \quad (3)$$

Thus the quantity on the left is independent of the time  $t$ .

This equation leads at once to the reciprocal relations discussed above in §§ 6 ... 11. For instance, let all the variations  $\delta'$  of the initial coordinates and momenta be zero except  $\delta' a_i$ , and all the variations  $\delta$  of the final coordinates and momenta be zero except  $\delta q_j$ : we obtain

$$\delta' p_j \delta q_j = -\delta b_i \delta' a_i, \quad . \quad . \quad . \quad (4)$$

or

$$\frac{\delta' p_j}{\delta' a_i} = -\frac{\delta b_i}{\delta q_j}. \quad . \quad . \quad . \quad (5)$$

15. If in  $S_1$  we vary  $t$  and  $\tau$  to  $t+dt$  and  $\tau+\delta\tau$  we get, by the defining equation for  $S_1$ , (2) § 4,

$$\Delta S_1 = L \delta t - L_0 \delta \tau + \Sigma (p \delta q) - \Sigma (b \delta a), \quad . \quad . \quad (1)$$

where  $\Delta$  denotes the variation from the value of  $S_1$  for the times of starting and arrival,  $t$  and  $\tau$ , to that for the times  $t+\delta t$  and  $\tau+\delta\tau$ , and  $\delta q, \delta a$  are variations effected without change of  $t$  or  $\tau$ . The insertion of the values of  $L$  and  $L_0$  gives this the form

$$\Delta S_1 = -H \delta t + H_0 \delta \tau + \Sigma (p \Delta q) - \Sigma (b \Delta a), \quad . \quad . \quad (2)$$

where

$$\Delta q = \delta q + \dot{q} \delta t, \quad \Delta a = \delta a + \dot{a} \delta t.$$

Taking successive variations  $\Delta, \Delta'$  and again  $\Delta', \Delta$ , and subtracting we get an extension of Lagrange's theorem in the forms

$$\begin{aligned} \delta' L \delta t - \delta L \delta' t + \Sigma (\delta' p \delta q - \delta p \delta' q) \\ = \delta' L_0 \delta \tau - \delta L_0 \delta' \tau + \Sigma (\delta' b \delta a - \delta b \delta' a), \quad . \quad . \quad (3) \end{aligned}$$

and

$$\begin{aligned} \Sigma (\Delta' p \Delta q - \Delta p \Delta' q) + \Delta' H \delta t - \Delta H \delta' t \\ = \Sigma (\Delta' b \Delta a - \Delta b \Delta' a) + \Delta' H_0 \delta \tau - \Delta H_0 \delta' \tau. \quad (4) \end{aligned}$$

This form of the theorem is given by Routh (Adv. Rigid Dynamics, § 479) but is obtained by a different process. The mode of derivation of the theorem (in the ordinary and in the extended form) from the Hamiltonian function seems to be the simplest possible.

16. If besides forces due to a function  $V$  which depends on the coordinates  $q_1, \dots, q_k$  of the system considered, there are forces,  $Q$ , independent of these coordinates (it may be which are functions of the unknown configurational coordinates of another system) but involve, perhaps, the time, the typical Lagrangian equation for such a case is

$$\frac{d}{dt} \frac{\partial T}{\partial \dot{q}} - \frac{\partial T}{\partial q} = - \frac{\partial V}{\partial q} + Q, \quad . \quad . \quad . \quad (1)$$

where  $T$  is a function of  $t$ , the  $q$ 's, and the  $\dot{q}$ 's. If, as in what goes before,  $H$  denote  $\Sigma(p\dot{q}) - T + V$ , and be expressed in terms of  $t$ , the  $q$ 's, and the  $p$ 's, it corresponds to the two equations

$$\frac{dp}{dt} = - \frac{\partial H}{\partial q} + Q, \quad \frac{dq}{dt} = \frac{\partial H}{\partial p}, \quad . \quad . \quad . \quad (2)$$

or if  $H' = H - \Sigma(Qq)$

$$\frac{dp}{dt} = - \frac{\partial H'}{\partial q}, \quad \frac{dq}{dt} = \frac{\partial H'}{\partial p}. \quad . \quad . \quad . \quad (3)$$

The part  $H' - H$  is of course here supposed left in the form  $-\Sigma(Qq)$ . The Hamiltonian differential equation for this case is

$$\frac{\partial S}{\partial t} + H' = 0, \quad . \quad . \quad . \quad . \quad (4)$$

where  $H'$  is expressed in terms of  $q_1, q_2, \dots, q_k, t$  and constants. As before the values of the  $p$ 's are given by equations of the type

$$p = \frac{\partial S}{\partial q}. \quad . \quad . \quad . \quad . \quad (5)$$

It is interesting to notice that Hamilton's principle and Lagrange's variational equation and therefore also the reciprocal theorems given above, remain unaffected by the change in  $S$ . We take  $S_1$  as given by the equation

$$S_1 = \int_{\tau}^t \{ \Sigma(p\dot{q}) - H + \Sigma(Qq) \} dt. \quad . \quad . \quad . \quad (6)$$

Since  $S$  is a function of the  $q$ 's, the  $\alpha$ 's, and  $t$ , we have when  $t$  and  $\tau$  are unvaried,

$$\delta S_1 = \Sigma \left( \frac{\partial S_1}{\partial q} \delta q \right) + \Sigma \left( \frac{\partial S_1}{\partial a} \delta a \right) = \Sigma(p \delta q) - \Sigma(b \delta a), \quad (7)$$

which is again (1) of § 13. It follows that  $S_1$  is here also stationary with respect to paths which nearly coincide with the actual trajectory and lie between the same terminal points.

The analysis for this more general case is thus in all respects the same as before, provided we use  $H' = H - \Sigma(Qq)$  instead of  $H$ , and, if required,  $L' = L + \Sigma(Qq)$  instead of  $L$  (see § 13) as the value of the so-called kinetic potential.

17. So far no use has been made in these variations of the second Hamiltonian function  $S'_1$ , defined by the equation

$$S'_1 = \int_{\tau}^t \{ \Sigma(\dot{p}q) + H \} dt. \quad . \quad . \quad . \quad (1)$$

This gives for a varied trajectory

$$\delta S'_1 = \Sigma \left( \frac{\partial S'_1}{\partial p} \delta p \right) + \Sigma \left( \frac{\partial S'_1}{\partial b} \delta b \right) = \Sigma(q \delta p) - \Sigma(a \delta b), \quad (2)$$

when  $S'_1$  is expressed in terms of the  $p$ 's and the  $b$ 's.

18. Let now  $A$  be defined by the equation

$$A = S_1 + \int_{\tau}^t H dt, \quad . \quad . \quad . \quad (1)$$

then we have

$$A = \int_{\tau}^t \Sigma(p \dot{q}) dt = \Sigma(\int p dq). \quad . \quad . \quad . \quad (2)$$

$A$  is what is usually called the *action* for the motion from the epoch  $\tau$  to the epoch  $t$ . It may be described either as the time integral of  $\Sigma(p\dot{q})$  [which, when  $T$  is a homogeneous quadratic function of the  $\dot{q}$ 's, is  $2T$ ] or as the sum of the displacement integrals of the  $p$ 's.

Integrating in (1) by parts we get

$$A + \int_{\tau}^t t \frac{dH}{dt} dt = S_1 + Ht - H_0\tau, \quad . \quad . \quad . \quad (3)$$

where on the right  $H$  refers to the epoch  $t$ . From this we

obtain by variation, and substitution for  $\delta S_1$  from (7), § 16,

$$\delta \left( A + \int_{\tau}^t t \frac{dH}{dt} dt \right) = t \delta H - \tau \delta H_0 + \Sigma(p \Delta q) - \Sigma(b \Delta a), \quad (4)$$

where as before

$$\Delta q = \delta q + \dot{q} \delta t, \quad \Delta a = \delta a + \dot{a} \delta t.$$

If at time  $t$ , and at time  $\tau$ , the configuration of the system be the same for both paths, we have

$$\delta \left( A + \int_{\tau}^t t \frac{dH}{dt} dt \right) = t \delta H - \tau \delta H_0; \quad . \quad . \quad . \quad (5)$$

and if, further, the terminal values of  $H$  be the same for both paths, we obtain

$$\delta \left( A + \int_{\tau}^t t \frac{dH}{dt} dt \right) = 0. \quad . \quad . \quad . \quad (6)$$

The quantity

$$A + \int_{\tau}^t t \frac{dH}{dt} dt$$

is thus stationary in value for different paths of transition adjacent to the actual path taken under the forces derived from  $L$ . If  $H$  is constant during the transition, that is if there is conservation of energy, the conclusion is that  $A$  is stationary in value for different paths of transition adjacent to the actual path. This is the principle of least action.

It is to be observed that it is not assumed that the time of passage is unvaried when adjacent paths are referred to in the statement of the principle: the condition imposed is the constancy of  $H$ . The value of  $A$  is then connected with the Hamiltonian function  $S_1$  by the equation

$$A = S_1 + H(t - \tau). \quad . \quad . \quad . \quad (7)$$

18. With regard to systems which are not holonomous, the use of the Hamiltonian function  $S$  shows that Hamilton's principle holds without alteration of form for such systems. Here the  $q$ 's are connected by non-integrable differential relations of the form

$$\alpha_{1i} \delta q_1 + \alpha_{2i} \delta q_2 + \dots + \alpha_{ki} \delta q_k + \alpha_i \delta t = 0, \quad . \quad . \quad (1)$$

of which there is a smaller number than  $k$ . If the



coordinates were independent we should have equations of the type

$$\frac{\partial S}{\partial q} = p, \quad \frac{\partial S}{\partial a} = -b. \quad . \quad . \quad . \quad . \quad (2)$$

But now we have at time  $t$  equations of the type

$$\frac{\partial S}{\partial q_i} = p_i + \lambda_1 \alpha_{i1} + \lambda_2 \alpha_{i2} + \dots + \lambda_m \alpha_{im}, \quad . \quad . \quad (3)$$

$$\frac{\partial S}{\partial a_i} = -b_i + \mu_1 \beta_{i1} + \mu_2 \beta_{i2} + \dots + \mu_m \beta_{im}, \quad . \quad (4)$$

where  $\lambda_1, \lambda_2, \dots, \mu_1, \mu_2, \dots$ , are undetermined multipliers. Thus for a variation from the actual to an adjacent succession of positions without change of  $t$  or  $\tau$ , we obtain

$$\delta S = \Sigma \left( \frac{\partial S}{\partial q} \delta q \right) + \Sigma \left( \frac{\partial S}{\partial a} \delta a \right) = \Sigma (p \delta q) - \Sigma (b \delta a), \quad . \quad (5)$$

as in the case of a holonomous system. The only difference is that in this case, while the variations from the actual path are all possible, the succession of positions given by these variations is not in general a possible path.

For the more general variation, as in § 15 above, the result is also the same as that for a holonomous system, with the difference just stated.

19. The question of permanence of canonical form, for changes of the  $(p, q)$  variables, has been discussed by various writers, from the point of view of the theory of contact transformations originated and worked out by Lie\*. The use of Hamilton's function adds clearness to this mode of considering the subject.

If the variables of the type  $p, q$  be changed to others of the type  $p', q'$  which are functions of  $p, q$  but not of  $t$ , and the condition

$$\Sigma p' dq' - \Sigma p dq = dW, \quad . \quad . \quad . \quad . \quad (1)$$

that  $dW$  be an exact differential when expressed in terms of the  $p$ 's and the  $q$ 's, be fulfilled, the change is called a contact transformation. We suppose for the present that there are  $2k$  independent equations connecting the variables  $p', q'$  with the variables  $p, q$ , and that  $W$  has by means of these been

\* See an excellent account by Lovett in the 'Quarterly Journal of Mathematics,' of Lie's remarkable dynamical paper in the *Archiv for Mathematik og Naturvidenskap*, vol. ii., Christiania, Jan. 1877.

converted into a function of the  $q'$ 's and the  $q$ 's. Equation (1) then gives

$$p' = \frac{\partial W}{\partial q'}, \quad p = -\frac{\partial W}{\partial q}, \quad . \quad . \quad . \quad . \quad (2)$$

and there are  $2k$  such equations.

But by the Hamiltonian differential equation

$$\Sigma p dq - H dt = dS, \quad . \quad . \quad . \quad . \quad (3)$$

where  $dS$  is a complete differential of a function of the  $q$ 's,  $t$ , and  $k$  constants (the  $a$ 's say), we have

$$p = \frac{\partial S}{\partial q}, \quad H = -\frac{\partial S}{\partial t}. \quad . \quad . \quad . \quad . \quad (4)$$

Hence, if we add (1) and (3) together we obtain

$$\Sigma p' dq' - H dt = d(W + S). \quad . \quad . \quad . \quad . \quad (5)$$

Since  $-p + \partial S / \partial q$ , that is  $\partial(W + S) / \partial q = 0$ ,  $W + S$  does not contain  $q$ , and is now an exact differential of the variables  $(q', t)$ , so that

$$p' = \frac{\partial(W + S)}{\partial q'}, \quad -H = \frac{\partial S}{\partial t} = \frac{\partial(W + S)}{\partial t}. \quad . \quad (6)$$

We infer that if  $H$  be expressed as a function of the variables  $(p', q', t)$ , we shall have the equations of motion in the canonical form

$$\frac{dp'}{dt} = -\frac{\partial H}{\partial q'}, \quad \frac{dq'}{dt} = \frac{\partial H}{\partial p'}. \quad . \quad . \quad . \quad . \quad (7)$$

The permanence of the canonical form of the equations of motion in any contact transformation of variables, and the identity of the function  $H$  for both sets of variables are thus established. The Hamiltonian principal function  $S'(q', a', t)$  [not to be confounded with the second Hamiltonian function referred to several times above] is given by the equation

$$S'(q', a', t) = W(q', q) + S(q, a, t). \quad . \quad . \quad . \quad (8)$$

The  $k$  constants  $a'$  may be regarded as corresponding to the  $a$ 's as the  $q'$ 's correspond to the  $q$ 's. The partial differential equation is

$$\frac{\partial S'}{\partial t} + H(q', a', t) = 0. \quad . \quad . \quad . \quad (9)$$

As an example we take the simple case of  $v' = q$ ,  $q' = -p$ . We obtain

$$\Sigma p' dq' - \Sigma p dq = -\Sigma (q dp + p dq) + d\Sigma(pq), \quad (10)$$

and therefore  $S = S - \Sigma(pq)$  is the new principal function. This it will be seen is the second Hamiltonian function for the variables  $p$ ,  $q$ , with its sign changed.

20. The  $2k$  relations referred to above enable the  $2k$  quantities  $(p', q')$  to be found in terms of the  $2k$  quantities  $(p, q)$ , or the  $2k$  momenta  $(p', p)$  in terms of the  $2k$  coordinates  $(q', q)$ . This presupposes that there is no functional relation connecting the  $2k$  quantities  $(q', q)$ . Now a relation or relations of this kind may exist, that is, it may be possible to eliminate the  $p'$ 's and the  $p$ 's, from the  $2k$  equations which define the  $p'$ 's and the  $q'$ 's in terms of the  $p$ 's and  $q$ 's, so as to give equations of the form

$$\phi(q'_1, q'_2, \dots, q'_k, q_1, q_2, \dots, q_k) = 0. \quad (1)$$

If there are  $h$  such relations, then along with

$$\Sigma p' dq' - \Sigma p dq = dW = \Sigma \frac{\partial W}{\partial q'} dq' + \Sigma \frac{\partial W}{\partial q} dq, \quad (2)$$

where  $W$  is a function of the variables  $(q', q)$  we have

$$\left. \begin{aligned} \Sigma \frac{\partial \phi_1}{\partial q'} dq' + \Sigma \frac{\partial \phi_1}{\partial q} dq &= 0 \\ \dots\dots\dots \\ \Sigma \frac{\partial \phi_h}{\partial q'} dq' + \Sigma \frac{\partial \phi_h}{\partial q} dq &= 0 \end{aligned} \right\} \dots\dots\dots (3)$$

Hence if  $\lambda_1, \lambda_2, \dots, \lambda_h$  be undetermined multipliers we have

$$\left. \begin{aligned} p'_i &= \frac{\partial W}{\partial q'_i} + \lambda_1 \frac{\partial \phi_1}{\partial q'_i} + \dots\dots + \lambda_h \frac{\partial \phi_h}{\partial q'_i} \\ -p_j &= \frac{\partial W}{\partial q_j} + \lambda_1 \frac{\partial \phi_1}{\partial q_j} + \dots\dots + \lambda_h \frac{\partial \phi_h}{\partial q_j} \end{aligned} \right\} \dots\dots (4)$$

There are  $2k$  equations of this form for  $(p', p)$  and the  $h$  relations  $\phi_1 = 0, \dots, \phi_h = 0$ , so that the  $2k + h$  quantities, that is the momenta and the  $h$  multipliers, can be determined.

By the values of  $p'_i, p_j$  we have of course simply

$$\Sigma p' dq' - \Sigma p dq = dW. \quad (5)$$





Hence (9) becomes

$$\Sigma p' dq' - \left( H - \frac{\partial U}{\partial t} \right) dt = d(S + U). \quad (14)$$

But, since

$$p_j = - \frac{\partial U}{\partial q_j} = \frac{\partial S}{\partial q_j}, \quad (15)$$

we have

$$\frac{\partial (S + U)}{\partial q_j} = 0, \quad (16)$$

that is  $S + U$  is a function of  $(q', t)$ . Equation (14) is thus of the Hamiltonian form.

Writing as before

$$H' = H - \frac{\partial U}{\partial t}, \quad (17)$$

we may infer that the equations of motion for the transformed system are of the form given in (11).  $S + U$  is the principal function.

21. Let there be no  $\phi$ -relations, but let the equations connecting  $(p', q')$  with  $(p, q)$  involve the time  $t$  explicitly. Then  $\Sigma p' dq' - \Sigma p dq$  may be an exact differential of a function of the variables  $(p, q)$  only, when  $t$  is not varied. Hence when  $t$  is kept constant

$$\Sigma p' dq' - \Sigma p dq = dW - \frac{\partial W}{\partial t} dt, \quad (1)$$

where  $dW$  is an exact differential of a function of the variables  $(p, q, t)$ . When  $t$  is allowed to vary this equation becomes

$$\Sigma p' dq' - \Sigma p dq = dW + U dt, \quad (2)$$

where  $U$  is also a function of  $(p, q, t)$ .

Let now, by expression of the  $p$ 's in terms of  $(q', q, t)$ ,  $W$  and  $U$  be transformed to functions of  $(q', q, t)$ . It is manifest that  $-U$  then becomes the partial differential coefficient with respect to  $t$  of the transformed  $W$ , that is we have now

$$\Sigma p' dq' - \Sigma p dq + \frac{\partial W}{\partial t} dt = dW, \quad (3)$$

with

$$p' = \frac{\partial W}{\partial q'}, \quad p = - \frac{\partial W}{\partial q}, \quad U = - \frac{\partial W}{\partial t}. \quad (4)$$

But also

$$\Sigma p dq - H dt = dS, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where  $S$  is the principal function  $[S(q, t, a)]$  for the original variables. Adding (3) and (5) we get

$$\Sigma p' dq' - (H + U) dt = d(W + S). \quad . \quad . \quad . \quad . \quad (6)$$

But since  $-\partial W / \partial q = \partial S / \partial q$ , we have  $\partial(W + S) / \partial q = 0$ , that is  $q$  does not appear in the function  $W + S$ , and so we get the canonical equations

$$\frac{dp'}{dt} = -\frac{\partial(H + U)}{\partial q'}, \quad \frac{dq'}{dt} = \frac{\partial(H + U)}{\partial p'}. \quad . \quad (7)$$

The principal function is now  $W + S$ .

IV. *The Equations of Electrodynamics for Moving Ponderable Media and the Principle of Relativity.* By H. R. HASSÉ, M.A., M.Sc., Fellow of St. John's College, Cambridge; Fielden Lecturer in Mathematics, Manchester University\*.

I.

THE Theory of Relativity, as applied to Maxwell's equations of the æther, rests on the work of Larmor and Lorentz, who independently proved that the equations were invariant under a certain space-time transformation. The first attempt to extend this result to the case of ponderable media was made by Lorentz †, who in 1904 applied the same transformation to the case of a non-magnetizable dielectric in an investigation as to the possibility of there being a positive result for the Michelson-Morley experiment in the case of propagation through a dielectric.

The discovery of a complete scheme of electrodynamical equations which shall satisfy the Principle of Relativity for the case of uniform translation is due to Minkowski ‡, who obtained a scheme of equations of the electromagnetic field which differed from that given by Larmor and Lorentz. These latter equations were, however, soon afterwards shown to be also consistent with the demands of this principle.

In this part of the paper we shall examine the way in which Minkowski obtained his scheme of equations, in order to find a satisfactory method of making use of the principle of relativity.

\* Communicated by the Author.

† Proc. Acad. of Sciences of Amsterdam, 1904, p. 809.

‡ *Göttinger Nachrichten*, 1908, reprinted in *Math. Ann.* vol. lxiii. (1910). References will be made to the reprint.

The conclusion arrived at is that it is not possible to deduce a *unique* system of electrodynamical \* equations for matter *in motion* by means of the principle of relativity, the corresponding equations for matter *at rest* being assumed to be known. In other words, the knowledge of the electrodynamical equations for matter at rest, which we may deduce from experimental evidence and not necessarily from any theory of the constitution of matter, together with the principle of relativity is not sufficient for the deduction of the equations of electrodynamics for matter in motion.

We can, however, make use of the principle of relativity in the following form. Having found from certain physical conceptions † the equations of the electromagnetic field for matter *in motion*, we may apply the transformations of the principle of relativity to deduce the constitutive relations which complete the scheme of electrodynamical equations. Such a deduction is applicable *only* to such cases of motion as are given by the particular transformation used, always transforming from matter in motion to matter at rest. In the form in which this principle would now be used, it might perhaps be better expressed as the hypothesis of the *null influence of the Earth's motion on optical and electrical phenomena*, in which form it is based directly on experimental evidence. For the equations of the electromagnetic field given by Larmor and Lorentz the problem as above stated was solved independently by the author‡ *for the case of uniform translation*, the constitutive relations necessary to complete the scheme of equations being derived by means of the above hypothesis.

In the general case of a variable velocity we should start from the equations of the field for matter in motion, referred to space-time coordinates  $x, y, z, t$ , and apply to them the necessary transformation to bring a particular point to rest referred to a system of coordinates  $x_1, y_1, z_1, t_1$ . The known constitutive relations for matter at rest in this space would then transform back into the required constitutive relations

\* The term "electrodynamical equations" is to be understood to include two groups, viz. "the equations of the electromagnetic field" and the "constitutive relations."

† *E. g.*, the equations of Larmor and Lorentz, based on the conception of matter made up of discrete electrons; or Walker's equations based on the conception of polarizations.

‡ Proc. Lond. Math. Soc. ser. 2, vol. viii. (1910). Deduced also from Minkowski's work by Mirimanoff, *Annalen der Physik*, vol. xxviii. (1909) p. 192.

in the  $x, y, z, t$  space. The method of course depends on a knowledge of the transformation\*.

A different method has been used by Cunningham†. He obtains the constitutive relations for matter in motion with a uniform velocity by an averaging process, using the Larmor-Lorentz transformation when dealing with the electrons themselves. There is no essential difference in the two methods as they both depend on a knowledge of the transformation required to reduce a particular point in motion to a point at rest.

The particular point which is to be emphasized is that the principle of relativity can in no way supersede any theory of the constitution of matter. The well-known transformation of Larmor and Lorentz is, as Minkowski remarked, essentially a mathematical deduction from the differential equation

$$\nabla^2\phi = \frac{1}{c^2} \frac{\partial^2\phi}{\partial t^2},$$

for the propagation of waves with the velocity of light, and quite independent of any theory of the propagation.

On the other hand, the principle of relativity can be used in order to obtain the constitutive relations necessary to complete the scheme of electrodynamical equations, the equations of the electromagnetic field for matter *in motion* having been previously deduced from some theory of the constitution of matter‡, such constitutive relations being limited in their application by the transformation used.

## § 1.

Minkowski's method depends on the following three axioms§.

1. If a single point of the matter is momentarily at rest, so that the vector  $w$  for that point is null—the surrounding

\* The general form of the transformation for the simplest case of accelerated motion so far investigated is given in a recent paper by the author, "The Equations of the Theory of Electrons transformed relative to a system in accelerated motion," Proc. Lond. Math. Soc. ser. 2, vol. xii. (1913).

† E. Cunningham, "The Application of the Mathematical Theory of Relativity to the Electron Theory of Matter," Proc. Lond. Math. Soc. ser. 2, vol. x. (1911).

‡ It is much more difficult to obtain the constitutive relations for matter in motion than to obtain the equations of the electromagnetic field. Cf. Larmor, 'Æther and Matter,' p. 113, where the constitutive relations given are stated only to be correct to the first order of the ratio of the velocity of the matter to that of light.

§ *Loc. cit.* § 8, p. 489.



medium moving in any manner whatever,—then for that particular point at the particular instant the relations between the various vectors are given by Maxwell's electrodynamical equations for matter at rest.

2. The velocity of matter is always less than that of light.

3. The general equations of the electromagnetic field are of such a nature that, for any "Lorentz-Transformation" of the space and time coordinates, the resulting equations contain the transformed vectors in the same manner as the original equations contain the original vectors, the different sets of vectors being related to each other in a certain definite manner\*.

This last axiom is called the principle of relativity.

Since Minkowski only applies his axioms to the case of media in uniform motion, the first axiom can be replaced by the following:—For media at rest the equations of the electromagnetic field are the ordinary Maxwellian differential equations, and further, the equations connecting the different vectors are the constitutive relations of the ordinary type. In this form the axiom needs no comment, nor does the second axiom. As to the third axiom, we must notice (1) that the "Lorentz-Transformation" only applies to the case of uniform motion in a straight line so that Minkowski's resulting equations only hold for this case †, and (2) that the definite manner in which the different sets of vectors are related depends on the above transformation; and therefore the connexion between them is only defined for the case of a constant velocity when the transformation is linear ‡.

We shall follow Minkowski's method of deriving his equations, and to this end we consider a space  $x, y, z$  in which matter is in motion at time  $t$  with a constant velocity  $w$  parallel to the axis of  $x$ . We may then apply the transformation

$$x = \epsilon (x_1 + wt_1), \quad y = y_1, \quad z = z_1, \quad t = \epsilon (t_1 + wx_1), \quad . \quad (1)$$

where  $\epsilon^2 \equiv (1 - w^2)^{-1}$ , the velocity of light being unity, to obtain a point  $x_1, y_1, z_1$  at rest in the second space corresponding to the moving point  $x, y, z$  in the first space.

Since the matter is at rest in the  $x_1, y_1, z_1, t_1$  space the electrodynamical equations are, according to the first axiom,

\* *Loc. cit.* § 5, p. 483, Definition of "Raum-Zeit-Vektor I. und II. Art."

† This obvious limitation does not seem to be sufficiently recognized, since Minkowski's equations have been freely applied in the case of a variable velocity. See note at the end of the paper.

‡ *Loc. cit.* p. 484.

given by the Maxwellian equations of the field

$$\left. \begin{aligned} \text{curl}_1 H_1 &= \frac{\partial D_1}{\partial t_1} + J_1, & \text{div } D_1 &= \rho_1 \\ \text{curl}_1 E_1 &= -\frac{\partial B_1}{\partial t_1}, & \text{div } B_1 &= 0 \end{aligned} \right\} \dots \quad (2)$$

together with the constitutive relations in the form

$$D_1 = K_0 E_1, \quad B_1 = \mu_0 H_1, \quad J_1 = k_0 E_1, \quad \dots \quad (3)$$

where the symbols have their usual meanings,  $J_1$  being the true electric current and equal to the conduction current  $C_1$  for matter at rest, and  $k_0$  the conductivity of the medium.

Now transform back again to the original  $x, y, z, t$  space by the transformation

$$x_1 = \epsilon(x - wt), \quad y_1 = y, \quad z_1 = z, \quad t_1 = \epsilon(t - wx),$$

obtained by solving equations (1), and by the third axiom we shall obtain the electrodynamical equations for matter in motion with a constant velocity  $w$  in the form

$$\left. \begin{aligned} \text{curl } Q &= \frac{\partial R}{\partial t} + K, & \text{div } R &= \tau \\ \text{curl } F &= -\frac{\partial G}{\partial t}, & \text{div } G &= 0 \end{aligned} \right\} \dots \quad (4)$$

where the vectors  $F, G, Q, R, K$  are connected with  $F_1, D_1, H_1, B_1, J_1$  by the relations

$$\left. \begin{aligned} F &= \{1, \epsilon, \epsilon\} \{E_1 - [w, B_1]\} \\ G &= \{1, \epsilon, \epsilon\} \{B_1 + [w, E_1]\} \\ R &= \{1, \epsilon, \epsilon\} \{D_1 - [w, H_1]\} \\ Q &= \{1, \epsilon, \epsilon\} \{H_1 + [w, D_1]\} \\ K &= \{\epsilon, 1, 1\} \{J_1 + w\rho_1\} \\ \tau &= \epsilon\{\rho_1 + (w, J_1)\}. \end{aligned} \right\} \dots \quad (5)$$

and

Further, the constitutive relations (3) in the  $x_1, y_1, z_1, t_1$  space transform into

$$\left. \begin{aligned} R + [w, Q] &= K_0 \{F + [w, G]\} \\ G - [w, F] &= \mu_0 \{Q - [w, R]\} \\ K - w\tau &= k_0 \{\epsilon^{-1}, \epsilon, \epsilon\} \{F + [w, G]\} \end{aligned} \right\} \dots \quad (6)$$

which give the constitutive relations in the  $x, y, z, t$  space in which the matter is in motion with a constant velocity  $w^*$ .

\* Cf. Einstein and Laub, *Annalen der Physik*, vol. xxvi. (1908), where a derivation of Minkowski's equations is given.

## § 2.

We have now to decide what physical interpretation is to be attached to the symbols occurring in the equations of the electromagnetic field (4) and in the constitutive relations (6), for the final form of the electrodynamical equations for moving ponderable media depends entirely on the meanings given to the various quantities. The equations (4) have to satisfy two conditions, (*a*) for  $w=0$  they must reduce to the Maxwellian equations for matter at rest in which the physical interpretation of the symbols involved is definitely known, and (*b*) they must for the free æther reduce to the known equations for electromagnetic disturbance in that medium. The constitutive relations (6) must also be consistent for the case of the free æther, where  $K_0=\mu_0=1$ , and  $k_0=0$ .

These conditions are all satisfied if we put

$$\left. \begin{aligned} F &\equiv E + f_1(w, D-E, B-H, J-\rho w) \\ G &\equiv B + f_2(w, D-E, B-H, J-\rho w) \\ Q &\equiv H + f_3(w, D-E, B-H, J-\rho w) \\ R &\equiv D + f_4(w, D-E, B-H, J-\rho w) \\ K &\equiv J + f_5(w, D-E, B-H, J-\rho w) \\ \tau &\equiv \rho + f_6(w, D-E, B-H, J-\rho w) \end{aligned} \right\}, \quad \cdot \cdot \cdot \quad (7)$$

where  $E, H$  denote the electric and magnetic forces,  $B, D$  the magnetic induction and electric displacement respectively,  $\rho$  the true electric density, and  $J$  the true electric current. This latter is equal to the sum of the conduction current  $C$  and the convection current  $\rho w$ , so that

$$J = C + \rho w.$$

The vector functions  $f_1, f_2, \dots$  are to be so chosen that they vanish when  $w=0$ , and also when

$$D-E=B-H=J-\rho w=0,$$

*i. e.* vanish for media at rest and for the free æther, but are otherwise arbitrary. If the resulting electrodynamical equations are to be linear in the electric vectors involved, the functions  $f_1, f_2, \dots$  must further be limited so as to be linear functions of their nine electromagnetic variables.

The final equations of the electromagnetic field for media

moving with a constant velocity are therefore

$$\left. \begin{aligned} \text{curl } \{H + f_3\} &= \frac{\partial D}{\partial t} + \frac{\partial f_4}{\partial t} + J + f_5, \\ \text{curl } \{E + f_1\} &= -\frac{\partial B}{\partial t} - \frac{\partial f_2}{\partial t}, \\ \text{div } \{D + f_4\} &= \rho + f_6, \quad \text{div } \{B + f_2\} = 0. \end{aligned} \right\} \dots \quad (8)$$

The corresponding constitutive relations are obtained by substituting in equations (6) the expressions for  $F$ ,  $G$ ,  $Q$ ,  $R$ ,  $K$ , and  $\tau$  given in equations (7). It is clear that we have satisfied all the conditions given in Minkowski's three axioms, and that equations (8) are true in the two limiting cases of media at rest and free æther, regard being had to the conditions limiting the form of the functions  $f_1, f_2, \dots, f_6$ .

### § 3.

We have now to show that by suitable choice of these functions the equations of the electromagnetic field (8) can be made to agree with those given by various physicists.

(A) Minkowski obtains his equations by interpreting  $F$ ,  $R$ ,  $Q$ ,  $G$ ,  $K$ , and  $\tau$  as electric force, electric displacement, magnetic force, magnetic induction, true electric current, and density of true electricity respectively. This is equivalent to assuming that all the functions  $f_1, f_2, \dots, f_6$  are zero, and the equations of the field are then

$$\left. \begin{aligned} \text{curl } H &= \frac{\partial D}{\partial t} + J, \quad \text{div } B = 0 \\ \text{curl } E &= -\frac{\partial B}{\partial t}, \quad \text{div } D = \rho \end{aligned} \right\} \dots \quad (9)$$

The corresponding constitutive relations obtained from (6) and (7) are

$$\left. \begin{aligned} D + [w, H] &= K_0 \{E + [w, B]\}, \\ B - [w, E] &= \mu_0 \{H - [w, D]\}, \\ J - w\rho &= k_0 \{\epsilon^{-1}, \epsilon, \epsilon\} \{E + [w, B]\}. \end{aligned} \right\} \dots \quad (10)$$

(B) If we make

$$f_3 \equiv -[D - E, w]$$

and all the other functions zero, we obtain the equations of  
*Phil. Mag.* S. 6. Vol. 27. No. 157. Jan. 1914. E



the field in the form given by Larmor and Lorentz, viz.,

$$\left. \begin{aligned} \text{curl } H &= \frac{\partial D}{\partial t} + J + \text{curl } [P, w], & \text{div } B &= 0, \\ \text{curl } E &= -\frac{\partial B}{\partial t}, & \text{div } D &= \rho, \end{aligned} \right\} \quad (11)$$

where we define a new vector  $P \equiv D - E$ , and call it electric polarization.

The corresponding constitutive relations deduced from (6) and (7) are given by

$$\left. \begin{aligned} D + [w, H] + [w, [w, D - E]] &= K_0 \{E + [w, B]\}, \\ B - [w, E] &= \mu_0 \{H - [w, E]\}, \\ J - w\rho &= k_0 \{\epsilon^{-1}, \epsilon, \epsilon\} \{E + [w, B]\}. \end{aligned} \right\} \quad (12)$$

If we write out these equations in full, remembering that they are only true for a vector whose components are  $w, 0, 0$ , we should obtain them in the form given by the author\*.

(C) If we make

$$\begin{aligned} f_3 &\equiv -[D - E, w], \\ f_1 &\equiv +[B - H, w], \end{aligned}$$

and the other functions zero, we obtain the equations of the electromagnetic field in the form given by Walker†, which correspond to his hypothesis of "continuous polarization" in the æther and "molecular polarization" in the material medium. The corresponding constitutive relations differ from those used by Walker by terms of the second order in  $w$ , so that his system does not completely satisfy the principle of relativity.

\* Proc. Lond. Math. Soc. ser. 2, vol. viii. (1910) p. 190. Equations (10) and (11).

† G. T. Walker, "Aberration and the Electromagnetic Field," § 14. Walker refers his equations to axes moving with the matter, and introduces new vectors  $E' \equiv E + [w, H]$ ,  $H' \equiv H - [w, E]$ ; he also assumes symmetry as regards all electric and magnetic quantities. A system of electrodynamical equations of this type has been given by J. Ishiwara, "Bericht über die Relativitätstheorie," p. 621, *Jahrbuch der Radioaktivität*, vol. ix. 1912, in which the general question of the equations of electrodynamics for ponderable media is discussed. It is clear, however, that a great number of systems of equations could be obtained and that no one system is, from the standpoint of the principle of relativity, better than any other; it is only when we take account of some theory of the constitution of matter that we can attempt to decide between the various systems of equations.

It is of interest to note in passing that Minkowski's equations of the electromagnetic field are identical with those obtained by Walker from the hypothesis of "continuous polarization" both in the æther and in the material medium.

We have thus shown that Minkowski's method of applying the principle of relativity cannot lead to a unique system of electrodynamical equations for matter in motion, for we have no means of determining from the three axioms alone the functions  $f_1, f_2, \dots, f_6$ .

#### § 4.

If we remove the second restriction (*b*) on the functions  $f_1, f_2, \dots, f_6$  in (7), we can include in (8) the equations of the electromagnetic field for moving media as given by Hertz. These are, in our notation,

$$\text{curl } \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t} + \mathbf{J} + \text{curl } [\mathbf{D}, w],$$

$$\text{curl } \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} - \text{curl } [\mathbf{B}, w],$$

$$\text{div } \mathbf{D} = \rho, \quad \text{div } \mathbf{B} = 0.$$

On comparison with equations (8), these make  $f_2 = f_4 = 0$ ,

$$f_1 = -[\mathbf{D}, w], \quad f_3 = [\mathbf{B}, w],$$

so that the corresponding constitutive relations from (6) and (7) should be

$$\mathbf{D} + [w, \mathbf{H}] + [w, [\mathbf{w}, \mathbf{D}]] = \mathbf{K}_0 \mathbf{E},$$

$$\mathbf{B} - [w, \mathbf{E}] + [w, [\mathbf{w}, \mathbf{B}]] = \mu_0 \mathbf{H},$$

$$\mathbf{J} - \rho \mathbf{w} = k_0 \{\epsilon^{-1}, \epsilon, \epsilon\} \mathbf{E}.$$

These are of course different from the constitutive relations given by Hertz, but it is clear from the way in which they have been obtained that they satisfy the principle of relativity, and from this point of view complete a scheme of electrodynamical equations by adding on to Hertz's equations of the field the correct constitutive relations.

The above equations differ from those in § 3 (A) (B) (C) in that in Hertz's equations the free æther is not defined by

$$\mathbf{D} - \mathbf{E} = \mathbf{B} - \mathbf{H} = \mathbf{J} - \rho \mathbf{w} = 0,$$

and consequently not by

$$\mathbf{K}_0 = \mu_0 = 1, \quad k_0 = 0,$$

the æther in his theory being always in motion with the moving medium.

Nevertheless it is possible to construct as above the constitutive relations necessary to complete the scheme of electrodynamical equations, thus showing again that there is practically no limit to the numbers of schemes of electrodynamical equations which can be deduced by means of the principle of relativity alone, and that it is only by means of some theory of the æther and of the constitution of matter that we can decide between the various schemes.

## II.

The experimental evidence which has led to the formulation of the hypothesis that optical and electrical phenomena are independent of the direction of the motion of the earth through the æther, contains a special group of experiments which have dealt with the changes to be expected when light or electricity passes through a moving medium. There are three outstanding examples of this group, viz., the rotation of the plane of polarization by an active medium \*, the double refraction due to the motion of the medium †, and the electrical resistance of a moving medium ‡.

The theory of the last two experiments does not present any mathematical difficulties and the experimental results lead to the constitutive relations given above §. On the other hand, in the case of the rotation of the plane of polarization we have to deal with a more complicated constitutive relation, and since this case serves as a good illustration of the first part of this paper, we shall deal with it in detail.

For the purpose of finding the absolute value of the rotation of the plane of polarization, it is perhaps easier to work with the equations (11) referred to axes moving with the matter, so that putting

$$x' = x - wt, \quad y' = y, \quad z' = z, \quad t' = t \quad . \quad . \quad . \quad (13)$$

the circuital relations take the form

\* Lord Rayleigh, *Phil. Mag.* 1902, p. 215.

† Lord Rayleigh, *Phil. Mag.* 1902, p. 678; D. B. Brace, *Phil. Mag.* vii. 1904, p. 317.

‡ Trouton and Rankine, *Proc. Roy. Soc. A.* vol. lxxx. 1907-08, p. 420.

§ Equations (12), when  $B=H$ , since the medium is non-magnetic, and  $\rho=0$ .

$$\left. \begin{aligned} \text{curl}' H' &= \frac{\partial D}{\partial t'} = \frac{\partial E}{\partial t'} + \frac{\partial}{\partial t'} (D - E), \\ \text{curl}' E' &= -\frac{\partial H}{\partial t'}, \end{aligned} \right\}$$

where

$$E' \equiv E - [w, H], \quad H' \equiv H + [w, E], \quad \dots \quad (14)$$

and we have put  $J=0$ ,  $B=H$ , since we are dealing only with a crystalline medium.

Further, we can from equations (14) above replace  $E$  and  $H$  by their values in terms of  $E'$  and  $H'$ , viz.,

$$H = \epsilon^2 \{ H' + [w, E'] - w(w, H') \}$$

and

$$E = \epsilon^2 \{ E' - [w, H'] - w(w, E') \}.$$

If we now consider a plane wave of light travelling in the direction of motion of the medium, *i. e.* along the axis of  $x'$ , and assume

$$E' = E_0 e^{is(Vt' - x')}, \quad H' = H_0 e^{is(Vt' - x')},$$

so that  $V$  is the velocity of the wave relative to the medium, the circular relations above reduce to

$$\left. \begin{aligned} H_{0z} &= \epsilon^2 V E_{0y} + \epsilon^2 w V H_{0z} + \frac{1}{is} \frac{\partial}{\partial t'} (D_y - E_y) \\ -H_{0y} &= \epsilon^2 V E_{0z} - \epsilon^2 w V H_{0y} + \frac{1}{is} \frac{\partial}{\partial t'} (D_z - E_z), \\ -E_{0z} &= \epsilon^2 V H_{0y} - \epsilon^2 w V E_{0z} \\ E_{0y} &= \epsilon^2 V H_{0z} + \epsilon^2 w V E_{0y} \end{aligned} \right\}$$

while

$$E_{0x} = H_{0x} = 0.$$

If we eliminate  $H_{0y}$ ,  $H_{0z}$ , we have

$$\left. \begin{aligned} \frac{(1 - \epsilon^2 w V)^2}{\epsilon^2 V} E_{0y} &= \epsilon^2 V E_{0y} + \frac{1}{is} \frac{\partial}{\partial t'} (D_y - E_y) \\ \frac{(1 - \epsilon^2 w V)^2}{\epsilon^2 V} E_{0z} &= \epsilon^2 V E_{0z} + \frac{1}{is} \frac{\partial}{\partial t'} (D_z - E_z) \end{aligned} \right\} \dots \quad (15)$$

In order to proceed further, we must investigate the relation connecting  $D - E$  with  $E'$  for the case of matter in motion, and this is to be done by transforming the corresponding relation for matter at rest.



In order to include in the constitutive relations for matter at rest the phenomena of structural rotation and rotation due to an external magnetic field, the first equation in (3) must be modified by the addition of terms containing differential coefficients of the first order of the electric force  $E_1$ . Let us consider the case of a crystalline medium, and let the axes of coordinates coincide with what would be the axes of optical symmetry of the crystal if it were not optically active, then we have for matter at rest\*

$$D_1 = K_1 E_1 + \left[ L_1, \frac{\partial E_1}{\partial t_1} \right] + [J_1 \nabla_1, E_1]. \quad (16)$$

where  $K_1$ ,  $J_1$ , and  $L_1$  are vector constants, the latter being proportional to the external magnetic field, while  $J_1$  is the coefficient of structural rotation.  $K_1$  is not necessarily the specific inductive capacity, as this may be altered when the external magnetic field is put on, though only to the second order†.  $\nabla_1$  is the vector operator

$$\frac{\partial}{\partial x_1}, \frac{\partial}{\partial y_1}, \frac{\partial}{\partial z_1},$$

so that the last term in the above expression is a vector whose components are

$$J_{1y} \frac{\partial}{\partial y_1} E_{1z} - J_{1z} \frac{\partial}{\partial z_1} E_{1y}, \dots, \dots$$

We must first of all express the quantities  $D_1$  and  $E_1$  in terms of  $D$ ,  $E$ , and  $H$  by means of the equations (5), which for case (B) above may be written in the form

$$\left. \begin{aligned} E &= \{1, \epsilon, \epsilon\} \{E_1 - [w, B_1]\}, \\ B &= H = \{1, \epsilon, \epsilon\} \{B_1 + [w, E_1]\}, \\ D &= \{1, \epsilon, \epsilon\} \{D_1 - [w, H_1]\}, \\ H - [D - E, w] &= \{1, \epsilon, \epsilon\} \{H_1 + [w, D_1]\}. \end{aligned} \right\} \quad (17)$$

Solving for  $E_1$  and  $D_1$  we find

$$\begin{aligned} E_1 &= \{1, \epsilon, \epsilon\} \{E - [w, H]\} = \{1, \epsilon, \epsilon\} E', \\ D_1 &= \{1, \epsilon, \epsilon\} \{D - E[w, H] + [w, [D - E, w]]\} \\ &= \{1, \epsilon, \epsilon\} \{D - E - [w, [w, D - E]] + E'\}. \end{aligned}$$

\* Larmor, 'Æther and Matter,' Section iv. Chap. xii.

† Larmor, 'Æther and Matter,' p. 197.

Further, we must transform from differential coefficients with respect to  $x_1, y_1, z_1, t_1$ , to those with respect to the moving axes  $x', y', z', t'$  by combining equations (1) and (13), so that

$$x' = \epsilon^{-1}x_1, \quad y' = y_1, \quad z' = z_1, \quad t' = \epsilon(t_1 + wx_1),$$

whence

$$\frac{\partial}{\partial x_1} = \epsilon^{-1} \frac{\partial}{\partial x'} + \epsilon w \frac{\partial}{\partial t'}, \quad \frac{\partial}{\partial t_1} = \epsilon \frac{\partial}{\partial t'}, \dots\dots\dots$$

After some algebraic work, equation (16) transforms into

$$\mathbf{D} - \mathbf{E} = (\mathbf{K}' - 1)\mathbf{E}' + \epsilon^2 \left[ \mathbf{L}', \frac{\partial \mathbf{E}'}{\partial t'} \right] + [\mathbf{J}' \nabla', \mathbf{E}'] + \epsilon^2 \left[ \mathbf{J}' w, \frac{\partial \mathbf{E}'}{\partial t'} \right]. \quad (18)$$

where

$$\mathbf{K}' - 1 = (1, \epsilon^2, \epsilon^2)(\mathbf{K}_1 - 1), \quad \mathbf{L}' = (\epsilon, 1, 1)\mathbf{L}_1, \quad \mathbf{J}' = \epsilon \mathbf{J}_1.$$

The second and third equations in the above vector equation give

$$D_y - E_y = (\mathbf{K}_y' - 1)E_y' - \epsilon^2 L_{x'}' \frac{\partial E_{z'}'}{\partial t'} - J_{x'}' \frac{\partial E_{z'}'}{\partial x'} - \epsilon^2 J_{x'}' w \frac{\partial E_{z'}'}{\partial t'},$$

$$D_z - E_z = (\mathbf{K}_z' - 1)E_z' + \epsilon^2 L_{x'}' \frac{\partial E_{y'}'}{\partial t'} + J_{x'}' \frac{\partial E_{y'}'}{\partial x'} + \epsilon^2 J_{x'}' w \frac{\partial E_{y'}'}{\partial t'},$$

Therefore finally, on substituting in (15) for  $D_y - E_y$  and  $D_z - E_z$ , we have

$$\left[ \frac{(1 - \epsilon^2 w V)^2}{\epsilon^2 V^2} - (\epsilon^2 + \mathbf{K}_y' - 1) \right] E_{0y} = i s E_{0z} [J_{x'}' \epsilon^2 (1 - w^2 - w V) - L_{x'}' \epsilon^2 V]$$

$$\left[ \frac{(1 - \epsilon^2 w V)^2}{\epsilon^2 V^2} - (\epsilon^2 + \mathbf{K}_z' - 1) \right] E_{0z} = -i s E_{0y} [J_{x'}' \epsilon^2 (1 - w^2 - w V) - L_{x'}' \epsilon^2 V]$$

If we take the case of a uniaxial crystal and let its axis of rotation coincide with the axis of  $x'$ , *i. e.* with the direction of motion of the medium,  $\mathbf{K}_y' = \mathbf{K}_z' = \mathbf{K}$ , and the equation to determine  $V$  becomes

$$\left[ \frac{\epsilon^2 (1 - w^2 - w V)^2}{V^2} - (\epsilon^2 + \mathbf{K} - 1) \right] = \mp s [J_{x'}' \epsilon^2 (1 - w^2 - w V) - \epsilon^2 L_{x'}' V]. \quad (19)$$

We note in passing that if  $J_{x'}' = L_{x'}' = 0$ ,  $V$  is determined from the quadratic

$$(\mathbf{K} - 1)V^2 + (V + w)^2 = 1^*,$$

giving Fresnel's coefficient as the term of the first order

\* Putting  $V = U - w$ , this gives  $(\mathbf{K} - 1)(U - w)^2 + U^2 = 1$ , agreeing with Larmor, 'Æther and Matter,' p. 59,  $U$  being the absolute velocity of wave, and  $V$  its velocity relative to the medium, which is moving with a velocity  $w$ .

in  $w$ , and it is interesting to note that it is the specific inductive capacity perpendicular to the direction of motion of the medium which enters into the equation.

To find an expression for the angle of rotation from (19), we have

$$s = \frac{2\pi}{V\tau},$$

where  $\tau$  is the period of vibration, and is the same for both rays, whence we can easily show that the angle of rotation per unit length of the medium is

$$\theta = \frac{\pi}{\tau} \left( \frac{1}{V_2} - \frac{1}{V_1} \right),$$

$V_1$  and  $V_2$  being the velocities of the two waves\*.

Substituting for  $s$  its value  $\frac{2\pi}{V\tau}$ , and writing  $J$  for  $\frac{2\pi J_x'}{\tau}$ ,  $L$  for  $\frac{2\pi L_x'}{\tau}$ , then the equation (19) becomes a quadratic in  $\frac{1}{V}$ ; viz.,

$$\frac{1}{\epsilon^2 V^2} - \frac{2w - J}{V} - \{K + \epsilon^2 wJ + L\epsilon^2\} = 0,$$

so that

$$\frac{2}{\epsilon V} = \epsilon(2w - J) + \{\epsilon^2(2w - J)^2 + 4(K + \epsilon^2 wJ + L\epsilon^2)\}^{\frac{1}{2}},$$

the two different wave-velocities being obtained by giving positive and negative values to  $J$  and  $L$ .

Taking the case of a structural rotation alone  $L = 0$ , and we have

$$\frac{2}{\epsilon V_1} = \epsilon(2w - J) + \{4w^2\epsilon^2 + 4K + J^2\epsilon^2\}^{\frac{1}{2}},$$

$$\frac{2}{\epsilon V_2} = \epsilon(2w + J) + \{4w^2\epsilon^2 + 4K + J^2\epsilon^2\}^{\frac{1}{2}},$$

therefore

$$\frac{2}{\epsilon} \left( \frac{1}{V_2} - \frac{1}{V_1} \right) = 2\epsilon J,$$

and the rotation  $\theta$  is

$$\frac{\pi}{\tau} \left( \frac{1}{V_2} - \frac{1}{V_1} \right) = \frac{\pi}{\tau} J\epsilon^2 = \frac{2\pi^2}{\tau^2} J_x' \epsilon^2,$$

there being no need to consider the constant  $J_x'$  as small.

\* Lorentz, Proc. Roy. Acad. Sci. Amsterdam, 1901-02.

In the case of a magnetic rotation alone  $\mathbf{J}=\mathbf{0}$ , but the expression for the angle of rotation cannot be put so simply.

We have

$$\frac{2}{\epsilon} \left( \frac{1}{V_2} - \frac{1}{V_1} \right) = \{4w^2\epsilon^2 + 4K + 4L\epsilon^2\}^{\frac{1}{2}} - \{4w^2\epsilon^2 + 4K - 4L\epsilon^2\}^{\frac{1}{2}},$$

so that up to the first power in  $L$ , the rotation  $\theta$  is

$$\frac{\pi}{\tau} \frac{\epsilon^2 L}{(w^2\epsilon^2 + 4K)^{\frac{1}{2}}} = \frac{2\pi^2}{\tau^2} \frac{\epsilon^2 L_{\infty}'}{(4K + w^2\epsilon^2)^{\frac{1}{2}}}.$$

These expressions for the rotation are thus independent of the sign of  $w$ , i. e., are the same whether the medium moves in the same direction as the wave of light, or in the opposite direction. For a direction of the wave of light oblique to that of the motion of the earth, these same expressions for the rotation should be obtained in accordance with the hypothesis by means of which the constitutive relation (18) was obtained, though the analysis in any particular case would be rather heavy.

Manchester University,  
August 1913.

*Note added December 1913.*

I find that there is some difference of opinion as to what is the correct interpretation of Minkowski's own work in § 8 of his paper. It seems clear that he himself regarded his system of equations as true for any variable velocity. According to the interpretation given in § 1 above, Minkowski's equations are to be considered as *proved* only for a uniform velocity.

The matter may, however, be considered in the following way. The theory of relativity restricts the relations between the various vectors to be such as are invariant in regard to the particular transformations of the theory, and Minkowski's work thus *suggests* constitutive relations which are true for any variable motion. These, combined with the equations of the field obtained from some theory of the constitution of matter, would then form a scheme of electrodynamical equations which are universally valid.

In this case equations (9), (10) of § 3 would be universally true and would correspond to a theory of the constitution of matter as is developed in Minkowski's (posthumous) paper, with the particular definition of magnetization involved in that theory.



In the same way equations (11) and (12) would be universally true and would correspond to the theory of the constitution of matter given by Larmor and Lorentz.

The difference between the various schemes (A), (B), (C) is really only one of the definition of the vectors, and no experiment can, since all are consistent with the theory of relativity, decide what definition is to be considered correct.

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V. *On the Thermal Conductivity and Specific Heat of Granite and Basalt at High Temperatures.* By HORACE H. POOLE, M.A., B.Sc.\*

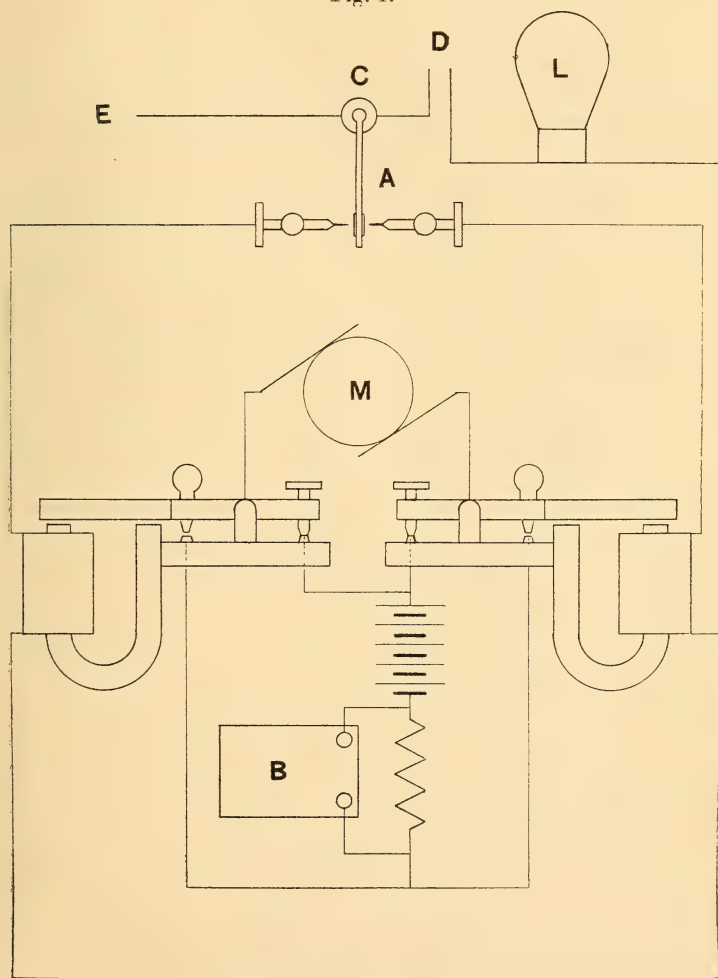
IN a previous paper (Phil. Mag. July 1912) a description was given of some experiments on the thermal conductivities of limestone and granite at high temperatures. The method adopted consisted in generating heat electrically along the axis of a cylinder of rock which is enclosed in a tube electric furnace maintained at a constant temperature, and measuring the difference of temperature between thermojunctions cemented in grooves cut at two distances from the axis. The results indicated a considerable fall of conductivity with rise of temperature in both cases. This fall was partly of a permanent nature due probably to a development of porosity in the limestone owing to escape of carbon dioxide, and to minute cracks in the granite. Both rocks showed signs of alteration, the granite being lighter in colour and much softer after heating. In addition to the permanent fall of conductivity there was a temporary fall at high temperatures, the conductivity rising again when the temperature was reduced. The determinations were carried up to  $366^{\circ}\text{C}$ . in the case of the limestone and  $537^{\circ}\text{C}$ . in the case of the granite.

In continuing the work it seemed to be desirable to make determinations on rock cylinders of greater ratio of length to diameter with a view to reducing possible end errors, accordingly the dimensions of the apparatus were modified. A new tube-furnace was constructed similar to the one previously described, except that the copper tube is longer and narrower—47 cm. long by 3.8 cm. in diameter. The furnace was laid horizontally. The heating element is composed of nichrome ribbon put on in two equal circuits, which can be joined either in series or parallel to facilitate the control of the temperature. This arrangement was, however, rendered unnecessary by the use of two transformers,

\* Communicated by the Author.

one of which was capable of yielding several ratios of transformation; and in the majority of cases the two circuits were connected in series, the pressures employed ranging from about 10 to about 40 volts. As before, the actual regulation is effected by means of a choking coil, but is rendered automatic by the arrangement shown in fig. 1.

Fig. 1.



A is a small metal arm about 1.8 cm. long, rigidly attached to the movable current coil of a wattmeter of the Siemens Dynamometer type, which measures the energy

supplied to the furnace; C is one of the mercury cups leading the current in and out; the wires D are connected to direct current 50 volt mains, and the contacts shown on either side of A with two small electromagnets whose armatures are, as shown, attached to Morse telegraph keys. These magnets contain a great number of turns of fine wire, so that they are energised by a very small current. The Morse keys are held in the position shown by light adjustable springs not shown in the diagram. L is a 16 C.P. 200-volt carbon lamp used as a high resistance. M is a permanent magnet motor, which is connected to a small windlass made out of an old clock from which is suspended the bundle of iron wires forming the core of the choking coil controlling the main alternating current.

The operation is as follows:—When the power is exactly equal to that for which the torsion head of the instrument is set, A is, as shown, midway between the platinum contact-pieces on either side; but if the power increases or decreases, A makes contact with one or other, thus energising the corresponding relay magnet and depressing the handle end of its Morse key, so that the local battery drives M one way or the other, thus raising or lowering the core of the choking coil until the power returns to the right value, when the key is released, thus short-circuiting the motor which stops very quickly. The use of a large voltage and very little current across the contacts at A makes the apparatus much more reliable, as contact is made more certainly and there is less sticking. For the most sensitive control the platinum wires constituting the contacts should be sharply pointed at the ends. This makes the contacts more reliable, but tends to cause sticking and consequent hunting; this was completely cured by suspending the buzzer B (an electric bell with the gong removed) from a small wooden arm attached to the wattmeter. When either key is depressed B commences to work, and the very slight vibration set up prevents any sticking of the platinum points. B was only added towards the end of the work, but is a distinct improvement. As the cup C forms part of both the direct and alternating circuits, it was found desirable to earth it at E through a fuse.

This apparatus worked most satisfactorily. The torsion head was set to the required reading and the apparatus left to adjust the power. The control could be made very close, as the gaps between A and the platinum contacts could be reduced to a small fraction of a millimetre.

As before, the energy developed in the central wire was

estimated by measuring the current and the potential difference between two points at a measured distance apart on it. As the distance between these points was considerably reduced and the diameter of the platinum wire was increased from 0.3 to 0.4 mm., the P.D.s to be measured never exceeded 1.8 volt, and thus could be directly read on a Tinsley potentiometer. This instrument was used for all the measurements, the "potential" terminals being directly connected to the thermo-couple key, before described, and never disturbed, and the "standard cell" terminals to a specially made switch such that connexion could be made either to the standard cell, or to the points on the central wire whose P.D. was required, or to the ends of a small standard resistance carrying the heating current, thus enabling the latter to be accurately measured. This switch could be turned so as to disconnect the "standard cell" terminals of the potentiometer from all conductors when the E.M.F.s of the couples were being measured. In this way the use of the potentiometer for measuring the energy supplied to the central wire in no way influenced the accuracy of its measurement of the small E.M.F.s of the couples. The original galvanometer was replaced by another giving a deflexion of about 0.5 scale-division per microvolt. This was amply sensitive and much more convenient to work with. For use in measuring the large P.D.s it could be shunted by means of a suitable switch.

The thermo-couples were, as before, made of platinum and platinum-iridium wires 0.1 mm. in diameter, the junctions being fused. Many of the junctions were formed by lightly twisting the ends together and then passing sparks from a coil to the tips. The wires were then untwisted, and a very small junction was the result. This is a very convenient method of electric welding small junctions, as the heat is developed exactly where it is required. The thermo-electric constants of the wire were obtained from the National Physical Laboratory, but as a larger number of points was found to be required for the accurate plotting of thermo-electric power against temperature, a couple made of the wires was placed in the furnace along with a platinum thermometer and accurately standardized. The figures so obtained agreed perfectly with those furnished by the N.P.L.

Two patent china cements named "Potmend" and "Cæmentium" were used in putting the rock cylinders together. The former, which can be made very thick, was found very convenient for filling the grooves, as it was not so hard as "Cæmentium" and so enabled the wires to be

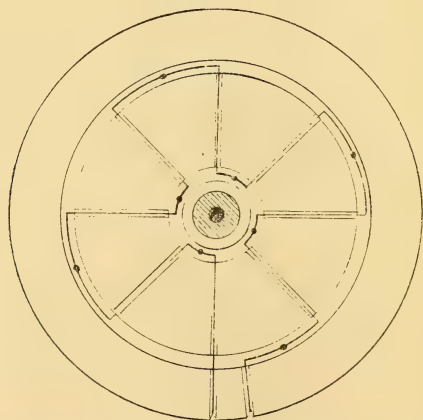


removed if breakages occurred. The latter cement was found best for cementing the rocks together. Both cements stood the high temperature well. As it seemed possible that the cements might attack the wires at high temperatures and alter their thermo-electric properties, one couple was tested after removal from the rock and found to be absolutely unchanged.

*First Basalt Experiment.*

It seemed to be desirable to measure the P.D. between two points on the central wire actually inside the rock cylinder, so as to eliminate errors due to want of uniformity of temperature and hence of resistance of the wire near the ends. Accordingly the cylinder was made in four pieces cemented together end to end. The length of each end piece was 8.9 cm. and of each centre piece 5.1 cm., so that the total length was 28.0 cm. As the diameter was only 3.67 cm., so that the cylinder fitted loosely inside the copper tube of the furnace, it would seem as if end effects must be negligible. The thermo-junctions measuring the mean temperature and the temperature gradient were sunk in grooves cut in the faces between the two central cylinders, which were ground to fit accurately together and joined by the thinnest possible layer of cement. The wires for measuring the potential gradient in the central wire were led in through

Fig. 2.



grooves cut in the inner faces of the end cylinders, and were fused to the central wire, these junctions being just at the ends of the central cylinders.

The arrangement of the couple for measuring the temperature gradient was very similar to that previously described and is shown in fig. 2, which is approximately to

scale. The circular grooves in which the junctions were situated, as shown, were about 2.5 mm. deep, the radial grooves being only about 0.5 mm., so that the disturbance of the heat-flow due to the latter was as small as possible. Unfortunately, the deep circular grooves could not be kept less than about 1.5 mm. wide at the top. As, however, the grooves were V-shaped and the junctions, which were kept as small as possible, were situated at the bottom of the V which was filled with cement, the groove ought not to introduce any large error.

The circular grooves were cut with carborundum powder by means of copper tubes of suitable diameter mounted on a drilling machine. The straight grooves were cut with a dentist's carborundum wheel.

The single junction for measuring the mean temperature was, as before, sunk in a straight groove cut in the opposite face.

Very great difficulty was experienced in boring small straight holes in the basalt, as the drill was inclined to bend and so increase the size of the hole as well as rendering it slightly crooked. The drilling was done by means of a soft-nosed twist drill, run the opposite way to the twist, and carborundum powder. The process was exceedingly slow, and the resulting hole was about 4 mm. in diameter and not as straight as it ought to have been. It was accordingly filled with cement which was allowed to set and then a hole 1.5 mm. in diameter drilled centrally through the comparatively soft cement.

An investigation on the error due to an unsymmetrical distribution of the cement round the central wire, or to eccentricity of the latter in the neighbourhood of the couples, indicated that this was very small owing to the use of four equally-spaced junctions.

A more dangerous source of error is possible want of uniformity of the cement layer at different points along the axis. This would cause variations in the temperature, and hence in the resistance per cm. of the central wire. There is in fact a sort of inherent instability, as, if the thermal insulation of the wire is greater at one point, there will be more heat generated there owing to the positive resistance temperature coefficient of platinum. This source of error would cause an apparent variation of conductivity with central current. A small variation of this kind was actually noticed, but was apparently due to potentiometer errors as will be explained later. For this reason, the same reliance cannot be placed on these results as on those of later determinations in which the chance of this error was greatly reduced.

The interior of the tube-furnace beyond the ends of the cylinder was filled with asbestos millboard soaked and made into a pulp with water, and the ends of the furnace were covered with a layer about 5 cm. thick of the same material. When this pulp dries it sets nearly as firm as the original millboard; unfortunately it contracts considerably in doing so, and was very liable to break the couple wires.

It was shown in a previous paper that

$$K = \frac{1}{\Delta} \left[ \frac{Q}{2\pi} \log_e \frac{r_2}{r_1} - \frac{C(r_2^2 - r_1^2)}{4} \cdot \frac{d\theta}{dt} \right]$$

very approximately, where

$K$  = Thermal conductivity.

$\Delta$  = Mean temperature difference indicated by the couple.

$Q$  = Heat flux in calories per second per cm. of the axis.

$r_1$  = Radius of the circle containing the inner junctions.

$r_2$  = " " " " outer " "

$C$  = Thermal capacity per c.c. of the rock.

$\theta$  = Average temperature of the rock.

The last term is only a small correction for any slight variations of temperature. The diameters of the grooves were 0.736 cm. and 2.60 cm. respectively. The distance of the single junction groove from the centre was 0.79 cm. This is so near the geometric mean of  $r_1$  and  $r_2$  that the temperature indicated by a couple in this groove may be taken as the mean temperature without appreciable error. For basalt  $C = 0.64$  about. The distance between the voltage leads on the central wire being 10.14 cm.,

$$Q = \frac{W}{10.14 \times 4.18}$$

where  $W$  is the product Current  $\times$  P.D. Putting in these figures we find

$$K = 4.73 \times 10^{-3} \times \frac{W'}{\Delta}$$

where

$$W' = W - 0.875\alpha,$$

$\alpha$  being the rate of rise of temperature in degrees per minute. It will be noticed that the correction for variation of temperature is very small,  $\alpha$  generally being of the order of 0.01 C. per minute; in fact, in the majority of cases it was negligible.

In arranging the rock cylinder in the furnace the single

couple was unfortunately broken, so that in the first set of determinations the average temperature was obtained from the reading of a couple placed in the narrow space between the cylinder and the inside of the copper tube, a suitable correction being added for the radial temperature gradient. In this and the later experiments tests were always made for leakage from the central wire to the couples. This was always inappreciable except at temperatures about  $600^{\circ}\text{C}$ . Tests were also made with the furnace at a steady high temperature and no central current, when  $\Delta$  was found to be zero as it should be. One, or occasionally two determinations were made per day. As the actual readings constituting a day's work were very similar to those obtained in the case of the granite determination, a sample of which is given later, there is no need to insert them here.

The daily mean results are shown in Table I. in chronological order, the symbols having the same meaning as before.

TABLE I. (Basalt.)

$\theta$ .	K.	W.	$\theta$ .	K.	W.	$\theta$ .	K.	W.
125° C.	5.22	2.45	68° C.	5.10	5.86	180° C.	4.82	5.38
40	5.00	2.32	68	4.91	3.60	295	4.61	5.27
99	5.03	2.34	69	4.88	2.85	265	4.85	6.92
52	5.08	3.43	70	5.01	4.56	146	4.88	7.07
155	5.13	3.41	69	5.15	5.78	133	4.99	8.60
180	5.17	2.83	133	5.19	5.42	104	5.07	8.98
319	4.93	2.52	131	5.61	2.85	222	4.75	7.75
233	5.20	2.56	143	4.88	5.55	339	4.60	7.46
278	4.81	4.14				378	4.53	7.27
62	4.98	4.20				431	4.43	7.21
298	4.95	4.01				500	4.32	6.79
						91	4.87	7.73
						190	4.70	7.33
						204	4.70	7.87

The values of K must be multiplied by  $10^{-3}$ .

The results in the first three columns are the first ones obtained; this set was brought to a conclusion by the breakage of one of the wires of the multiple couple. These results, which are not very consistent, are in marked contrast to those previously obtained for granite, as they show an apparent rise of conductivity with temperature up to about  $200^{\circ}\text{C}$ , above which a fall is shown.

The cylinders were taken to pieces and the couples remade, the single couple being placed in its proper groove, and the cylinders cemented together again and replaced in the furnace.



The distance between the P.D. leads on the central wire being only 10.00 cm., a suitable modification was made in the formula for  $K$ . The end spaces were on this and all subsequent occasions filled with quartz sand, and the ends as before covered with pulped asbestos. The next results obtained are shown in the next three columns. The first five results at approximately the same temperature show an apparent variation of  $K$  with  $W$ ; the next three were so inconsistent that it was evident that there must be some source of error. This was traced to the potentiometer. In this instrument the Thomson-Varley shunt is employed, and if the double contacts forming the ends of the shunt become at all foul, a small error in the reading is introduced. It appeared that this error, which was measured by cutting out the couple at the mercury key, might amount to about 15 or 20 microvolts. In all the previous basalt determinations  $W$  and hence  $\Delta$  were small, so that this source of error was important. The error, if it occurred at all, would have been far smaller in the determinations described in the previous paper, as in them the values of  $\Delta$  were much larger. In all subsequent work particular attention was paid to the double contacts, which were periodically cleaned with paraffin oil. This had the effect of reducing the error to about 1 or 2 microvolts, the residue probably being due to thermal effects at the terminals. After every reading of the E.M.F.s of the couples this small error was measured and corrected for. The effect of any remaining uncertainty was reduced by using larger values of  $W$ .

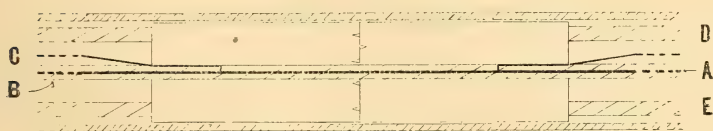
The subsequent results, shown in the last three columns of the table, quite contrary to the previous ones, show a steady fall of conductivity with rise of temperature. As this fall was expected, it was concluded at the time that the previous results were unreliable owing to the error just mentioned. However, another explanation of the discrepancy is possible and will be mentioned later. The determinations were brought to a conclusion by the breakage of the multiple couple.

#### *Second Granite Experiment.*

In constructing new granite cylinders, of medium-grained Newry granite, the cylinders were first roughly turned and then the central hole, 4.3 mm. in diameter, bored. The cylinders were then mounted on an axle through this hole and turned down to the required size, so that the hole was accurately centred when finished. Only two cylinders were employed as in the original determinations, their lengths

being 7.5 cm. and diameters 3.6 cm., so that the complete cylinder was 15.0 cm.  $\times$  3.6 cm., which was considered a sufficient ratio of length to diameter. The arrangement of the couples was identical with that used for the basalt. The arrangement of the P.D. leads connected to the central wire is shown in fig. 3, which shows a section of the rock-cylinder and furnace-tube. A is the platinum wire, B an asbestos lagging which fills the hole and keeps the wire

Fig. 3.



approximately central in it, and insulates A from the leads C everywhere, except at the junctions. This lagging was removed from an asbestos insulated heating wire and threaded onto the platinum wire. A more convenient method adopted when the cylinder was being put together a second time was that of unlaying a three-strand asbestos cord and relaying it carefully round the wire. The lagging was made as uniform as possible to prevent errors due to inequality of temperature of the central wire. The insulation was tested by passing a very small measured current through the central wire and measuring the P.D. between the leads C, hence the resistance of the part of the central wire between the leads was found; and as the current was too small to cause appreciable heating, this ought to agree with the known resistance of that length of wire at room temperature. This it was found to do almost exactly. Any fault in the insulation would thus have been detected. By this arrangement the P.D. junctions were inside the cylinder as required, while the extra end cylinders were dispensed with.

D and E are asbestos cords cemented to the cylinder as shown. The fine couple leads were twisted round these, and where they passed through the asbestos ends of the furnace another asbestos cord was wound round them. This arrangement entirely prevented breakage in the furnace ends and enabled the latter to be opened when necessary without breaking the wires. The difficulty of doing this previously to the adoption of this plan had greatly hindered the location of breakages in the couples. The couple grooves are also shown in section in the figure.

The distance between the P.D. junctions on the central wire was 10.0 cm.; the diameter of the outer groove was 2.61 cm. and that of the inner 0.725 cm.; so, taking  $C$  for granite as 0.53, we find that with the same notation as before,

$$K = 4.875 \times 10^{-3} \times \frac{W'}{\Delta} \quad \text{where } W' = W - 0.712 \alpha.$$

A specimen day's observations are shown in Table II.

TABLE II. (Granite).

T.	R.	V.	A.	W.	$E_1$	$\theta_0$ .	$E_2$ .	$\theta$ .	4P.	$\alpha$ .
9.5 A.M.	400	(turned on)								
11.47 "	340	.....	.....	.....	3120.5	15.6	3301	240		
1.4 P.M.	.....	1.3692	5.834	7.982	3064.5	16.7	3259	237.5	61.52	-0.0052
2.0 "	800	1.3686	5.836	7.981	3051	17.3	3254.5	237	61.50	
3.34 "	650	.....	.....	.....	5612	18.5	5822	400		
4.30 "	.....	1.4321	5.414	7.755	5548	19.4	5779.5	398	63.57	
6.8 "	.....	1.4309	5.418	7.752	5491	20.1	5728	395	63.53	+0.0059
6.40 "	.....	1.4306	5.416	7.748	5492.5	20.2	5731	395	63.53	

Here :—

T = Time at which reading of  $E_1$  was made.

R = Setting of regulating wattmeter in arbitrary units made *after* the corresponding readings had been taken. No entry is made when R was not changed.

V = P.D. between the leads in volts measured on the potentiometer.

A = Central current in amperes measured on the potentiometer.

W = VA = Power developed in the central wire between P.D. leads.

$E_1$  = E.M.F. of the single couple in microvolts.

$\theta_0$  = Temperature of the mercury key forming the cold junction of this couple.

$E_2$  = Calculated E.M.F. of this couple with its cold junction at 0°C., correction having been made for  $e$ .

$\theta_1$  = Temperature corresponding to  $E$  read from a curve. As the distance of the single junction from the centre was about 0.88 cm. which was greater than  $\sqrt{r_1 r_2}$ , a small correction depending on  $\Delta$  was added in reading off  $\theta$  so as to obtain the true mean temperature.

4P = Four times the thermo-electric power corresponding to  $\theta$  read from another curve.

$\alpha$  = Rate of rise of temperature in degrees per minute.

W' = Mean W - 0.712  $\alpha$ .

E<sub>3</sub> = E.M.F. of the multiple couple in microvolts.

Z = Open circuit reading of the galvanometer.

X = Reading of the galvanometer with the couple cut out and potentiometer set to 10 microvolts.

Y = Reading of the galvanometer with the couple cut out and potentiometer set to 110 microvolts.

TABLE II. (Granite).

W'.	E <sub>3</sub> .	Z.	X.	Y.	$e$ .	E <sub>4</sub> .	$\Delta$ .	K.	K'.
7.985	577	278.5	287.3	364.8	-1.5	578.5	9.40	4.14	4.15
	574	264.5	276.3	371.5	-2.5	576.5	9.37	4.15	
7.746	629	223.8	236.7	331.0	-3.5	632.5	9.95		3.845
	621	224.8	236.8	329.8	-3	624	9.82	3.85	
	621.5	224.3	237.0	331.0	-3.5	625	9.835	3.84	

Mean Results for the day:—K=4.15  $\times 10^{-8}$  at 237° C.

K=3.845  $\times 10^{-8}$  at 395° C.

$e$  = Potentiometer error =  $10 - 100 \times \frac{X - Z}{Y - X}$ . This could not be obtained directly as the potentiometer could not be set to less than about 5 microvolts.

E<sub>4</sub> = E<sub>3</sub> -  $e$ .

$\Delta$  =  $\frac{E_4}{4P}$ .

K = Conductivity calculated from a single set of readings neglecting  $\alpha$ .

K' = Conductivity calculated from W' and mean value of  $\Delta$  for two consecutive sets of readings.

It will be noticed that on this day on which two determinations were made, the correction for  $\alpha$  was quite negligible and that for  $e$  was smaller than other probable errors.

In attempting to obtain a determination at about 550° C the single couple broke. This must have been caused by thermal expansion of the rock as the couple joined again at temperatures below 400° C. The determinations were



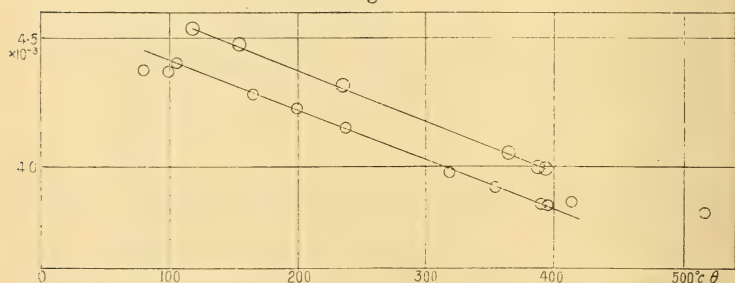
70 Mr. H. H. Poole on *Thermal Conductivity and Specific* accordingly continued, but that temperature could not be exceeded. The results are shown in Table III. in the first three columns.

TABLE III. (Granite).

$\theta$ .	K.	W.	$\theta$ .	K.	W.
105° C	$5.68 \times 10^{-3}$	7.657	115° C	$4.70 \times 10^{-3}$	8.105
87	5.655	5.905	387	3.995	7.708
154	5.50	12.10	235	4.315	7.980
98	5.20	7.265	154	4.475	8.099
346	4.265	7.341	117	4.535	8.271
516	3.82	7.212	364	4.05	8.086
105	4.40	7.330	393	3.99	7.740
413	3.86	7.284			
354	3.915	7.022			
99	4.37	7.097			
237	4.15	7.984			
395	3.845	7.746			
165	4.28	7.987			
79	4.375	4.607			
199	4.225	8.382			
318	3.975	8.206			
390	3.85	8.015			

The first four results are very high and decrease consecutively irrespective of the temperature. Heating to 346° C and then to 516° C caused a large drop. The remainder of the results are plotted in fig. 4 (small circles),

Fig. 4.



and lie very fairly along the line shown which represents  $K = (4.60 - 0.00192 \theta) \times 10^{-3}$ . The values obtained at 516° C. and at 413° C. lie as shown somewhat above this line: the latter determination was not a very satisfactory one as in it  $\alpha$  was 0° 216 C. per minute. There is no evidence of any apparent change of K with W; in fact the close agreement of the results at 99° C. and 79° C., in which the values of W were quite different, is quite satisfactory.

These values agree fairly well with the previous determinations on another granite cylinder, the chief point of difference being the straightness of the  $K : \theta$  line. The initial high results are somewhat higher than any previously obtained, but this is easily explained, as in the former work the rocks were initially heated to a fairly high and unknown temperature to bake the cement then used, so that even the first determination represented rock whose conductivity had already been permanently lowered by heat. In the present instance the cement used set without heat.

*Determination of Specific Heat.*

The equation

$$K = \frac{1}{\Delta} \left[ \frac{Q}{2\pi} \log_e \frac{r_2}{r_1} - \frac{C(r_2^2 - r_1^2)}{4} \frac{d\theta}{dt} \right],$$

which is true so long as  $\frac{d\Delta}{dt}$  is small compared with  $\frac{d\theta}{dt}$ , has been used above, an approximate value of  $C$  being employed in the small correction for any slow temperature variation. If, however, we make  $Q=0$ , *i. e.* turn off the central current and arrange that  $\frac{d\theta}{dt}$  is large, the equation becomes

$$K = - \frac{C(r_2^2 - r_1^2)}{4\Delta} \cdot \frac{d\theta}{dt}.$$

This equation, however, neglects the effect of the central hole. When this is taken into account the equation becomes

$$K = - \frac{C}{\Delta} \left[ \frac{r_2^2 - r_1^2}{4} - \left( \frac{R^2}{2} - \frac{H}{2\pi C} \right) \log_e \frac{r_2}{r_1} \right],$$

where  $R$  is the radius of the hole and  $H$  is the thermal capacity per cm. of the lagging and central wire. In the small correction for  $H$  we can substitute an approximate value of  $C$  without serious error. Substituting for  $R$  its value 2.15 mm. and making an estimation for  $H$  (which is of very small importance) we find that

$$K = -0.3698 \times \frac{C}{\Delta} \cdot \frac{d\theta}{dt},$$

or

$$\frac{C}{K} = -2.704 \times \frac{\Delta}{\frac{d\theta}{dt}}$$

the minus sign occurring since  $\Delta$  is always negative, *i. e.* the

interior of the rock is colder when the temperature is rising and *vice versa*. The correction for the central hole amounts to about 6 per cent.

From this equation, knowing  $K$ , we can find  $C$  and hence obtain the specific heat. Both rising and falling temperatures were employed, the observations with the latter being obtained at the conclusion of a determination of  $K$  by turning off the central and furnace currents and observing  $\theta$  and  $\Delta$  as the rock cooled. For observations with rising temperatures the furnace regulator was, at first, set to a definite value and observations taken as the temperature rose: as, however, the rate of rise becomes slower and slower as the temperature rises, it was found better to arrange a clock which slowly turned the torsion head of the regulator so as to increase the power; by this means the rate of rise was kept fairly uniform.

The method adopted in measuring  $\frac{d\theta}{dt}$  and  $\Delta$  was as follows:—At a given instant the E.M.F. of the single couple measuring  $\theta$  was read, then almost immediately afterwards the thermometer giving the temperature of the mercury key which forms the cold junction; the connexions of this key were then changed, the multiple couple being connected to the potentiometer and read exactly two minutes after the single couple, which was then read again at the end of another two minutes and so on. Thus readings of the single couple were obtained at exact intervals of four minutes with readings of the multiple couple at the middle of each interval.

Let  $\delta E_2$  be the difference between successive readings of the single couple corrected for the temperature of the key and potentiometer errors, and  $E_4$  be the reading of the multiple couple also corrected for potentiometer errors, then if  $P$  be the thermo-electric power corresponding to the mean temperature (which approximately corresponds with the temperature at which  $E_4$  was observed) the average value of  $\frac{d\theta}{dt}$  throughout the interval

$$= \frac{\delta E_2}{240P} \quad \text{and} \quad \Delta = \frac{E_4}{4P}, \text{ since there are four junctions;}$$

hence we find that

$$\frac{C}{K} = -162.2 \times \frac{E_4}{\delta E_2}.$$

The potentiometer was set at the commencement of a set of observations and the accuracy of the setting checked at the end. The variation was always negligible. The small potentiometer error before mentioned was measured before and after each series (there being no time to do so between the readings) and corrected for, any small variation in it being distributed according to the time. This correction was generally quite unimportant.

It will be noticed that each value of  $C$  is obtained from the difference between a pair of successive values of  $E_2$ , so that any error in taking a reading of  $E_2$  at the right instant will affect two successive values of  $C$  with errors of opposite sign. Theoretically it might be preferable to plot  $E_2$  against time and smooth out any irregularities in doing so, but in practice the above method was found more convenient. The irregularities occurring in individual values of  $C$  can be removed by taking means as there are a very large number of results available.

TABLE IV. (Granite).

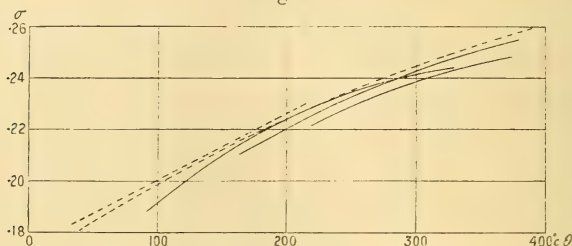
$E_1$ .	$\theta_0$ .	$e$ .	$E_2$ .	$-\delta E_2$ .	$E_3$ .	$E_4$ .	$\frac{C}{K}$ .	$\theta$ .	$K$ .	$S$ .
4611	18.9	-2.5	4833.5							
				252	248	250.5	152.0	330	3.97	.230
4358	19.0		4581.5							
				240.5	236	238.5	151.4	314	4.00	.230
4117.5	19.0	-2.0	4341							
				233	219	221	144.9	298	4.03	.222
3884	19.1		4108							
				214	201	203	144.9	284.5	4.05	.223
3669	19.2		3894							
				198	186	188	144.9	271	4.08	.225
3469	19.3		3696							
				187	170.5	172.5	141.0	258.5	4.10	.220
3282	19.3		3509							
				170	159.5	161.5	145.1	247	4.13	.226
3111	19.4		3339							
				173	147	149	131.6	236	4.15	.208
2938	19.4	-1.5	3166							
				160	138	139.5	133.2	225	4.17	.212
2778.5	19.4		3006							
				150	128	129.5	132.0	215.5	4.19	.211
2627.5	19.5		2856							

A few figures from one cooling determination are given in Table IV. The values of  $K$  used to find the specific heat  $S$  were calculated from the formula  $K = (4.60 - 0.00192\theta) \times 10^{-3}$ . The density of the rock was 2.625. The other symbols have the same signification as in Table II.



The results obtained from five series of observations are plotted in fig. 5. Each curve represents one series of observations. The individual values are not plotted as there were

Fig. 5.



so many of them that they would render the figure confused. The full line curves represent determinations on falling temperatures and the dotted curves those on rising temperatures: the shorter of the two latter represents a determination with a constant supply of energy to the furnace, the longer one in which the energy was slowly increased by the clock as before explained. From these curves means were taken, account being taken of the fact that at low temperatures the cooling determinations were less reliable owing to the slow rate of cooling and small temperature differences involved. These averages lie on the curve

$$S = 0.161 + 0.405 \times 10^{-3}\theta - 0.45 \times 10^{-6}\theta^2$$

which represents the mean results of these experiments between the temperatures 40° C. and 380° C.

#### *Further Experiments on the Granite Cylinder.*

The cylinder was taken to pieces and the single couple renewed. An attempt was made to prevent the wires from breaking at high temperatures by coating them with rubber solution before cementing them into the rock. It was hoped that when the rubber burnt away it would leave a minute air space, thus allowing the wire a certain amount of freedom. The single couple and the leads of the multiple couple were treated in this way. The multiple couple itself was not removed from the groove system in the rock face. Seven results were obtained which were very concordant with the exception of the first, which was slightly too high. These results are given in the last three columns of Table III. and are plotted in fig. 4 (larger circles). They lie very closely along the line  $K = (4.77 - 0.00198\theta) \times 10^{-3}$  and are thus nearly 4 per cent. higher than the previous ones.

Another set of determinations of the specific heat was also made, the procedure being the same as before. In working these out  $K$  was taken as  $(4.77 - 0.00198 \theta) \times 10^{-3}$ . Even so the mean value obtained

$$S = 0.154 + 0.335 \times 10^{-3} \theta - 0.25 \times 10^{-6} \theta^2$$

is somewhat lower than the previous one. This difference was chiefly due to low values obtained with heating experiments which on this occasion gave lower results than the cooling experiments. The latter gave values only slightly below the previous cooling determinations.

We may take as the mean of the determinations on the conductivity of this sample of granite

$$K = (4.68 - 0.00195 \theta) \times 10^{-3}.$$

This refers to granite that has been heated to  $500^\circ \text{C}$ .

As regards specific heat, the mean of the two formulæ already given is

$$S = 0.158 + 0.37 \times 10^{-3} \theta - 0.35 \times 10^{-6} \theta^2.$$

This gives a value  $0.178$  at  $56^\circ \text{C}$ . The mean of the specific heats of three granites obtained by Dr. Joly with the steam calorimeter between  $12^\circ \text{C}$ . and  $100^\circ \text{C}$ . is  $0.192$ , so that the above figures are probably about 8 per cent. too low; the method is probably more suitable for finding the variation of the specific heat with temperature than its absolute value. The rise of the specific heat of granite with rise of temperature accords well with the known rise for quartz and felspar.

### *Second Basalt Experiment.*

The arrangement of the rock cylinder adopted in making another set of determinations on basalt was somewhat different. The cylinder,  $18.2 \text{ cm}$ . long by  $3.6 \text{ cm}$ . diameter, was divided longitudinally instead of transversely. Grooves were cut along the axis of each half cylinder as shown in

Fig. 6.



fig. 6, thus forming a fine accurately centered hole when the two were cemented together, through which the central wire

passed. The P.D. wires lead in through grooves as shown at A and B. The multiple couple was sunk in a series of straight grooves as shown in the figure, in which half of the couple is seen, the other eight junctions being cemented into the opposite face. The grooves in the two faces were arranged so that the inner junctions on one face were opposite to the outer junctions on the other face and *vice versa*.

The transverse grooves in the two faces did not register with each other but were about 2 mm. apart, thus decreasing the chance of short circuit between different parts of the couple. All these grooves were considerably finer than shown in the figure, being about 0.6 mm. wide at the top. The longitudinal couple grooves were about 1.2 mm. deep, being V-shaped as before. The transverse and axial grooves were about 0.3 mm. deep. The couple passed under the central wire in one place as shown: here the transverse groove was made deeper and the couple insulated from the central wire by means of cement. The single couple is shown at C. The couple leads along the outside of the cylinders were only laid in their grooves, no cement being used. They were insulated from the copper furnace tube by thin mica sheet which was cemented over the whole cylinder. By this means all danger of these parts of the couples breaking was obviated, and for the first time no trouble of this kind occurred. The rest of the arrangements remained as before.

There are several advantages in dividing the rock longitudinally, chief of which is the smallness and accurate centering of the central aperture; all danger of want of uniformity of temperature of the central wire is eliminated and the mean heat flux from a length of about 6 cm. of it is taken. Another advantage is that the distance from the junctions to the radial grooves is about 7.5 mm. instead of 1.4 mm., as was the case for the inner junctions in the previous experiments. The use of eight pairs of junctions doubles the E.M.F. to be measured for a given value of  $\Delta$ , which is also an advantage.

The distances of the bottoms of the inner and outer grooves from the centre being 0.493 cm. and 1.464 cm. respectively and the distance between the P.D. wires 10.5 cm., we find that with the same notation as before

$$K = 4.007 \times 10^{-3} \times \frac{W'}{\Delta},$$

where

$$W' = W - 1.286 \alpha.$$

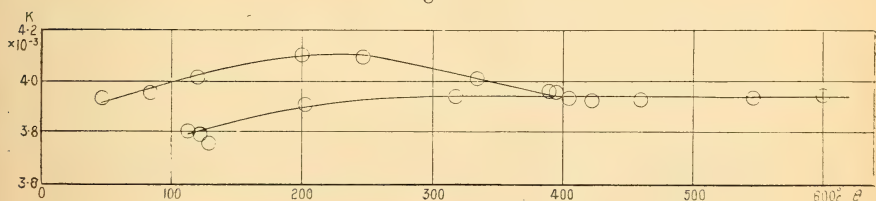
As the actual observations and method of computation closely resembled the previous ones, there is no need to give another example. The only variation consisted in the insertion of a reversing key in the central circuit. This was needed to obtain a satisfactory determination at 600° C., as about that temperature leakage through the red-hot rock begins to cause trouble. Reversing the central wire current caused an immediate change of about 20 microvolts in the apparent E.M.F.s of the couples, so that readings were taken with the central current flowing both ways, and the means used. This was quite unnecessary at lower temperatures, as then the insulation was quite satisfactory.

The results are shown in Table V. and plotted in fig. 7.

TABLE V. (Basalt).

$\theta$ .	K.	W.	$\theta$ .	K.	W.
47° C.	$3.935 \times 10^{-3}$	2.95	318° C.	$3.94 \times 10^{-3}$	7.47
84	3.955	6.12	395	3.955	7.90
110	4.015	7.93	460	3.93	7.68
200	4.10	8.04	122	3.795	8.00
247	4.095	8.06	547	3.935	8.20
335	4.01	7.97	129	3.76	8.29
390	3.96	7.77	422	3.925	8.21
113	3.805	7.52	600	3.945	7.90
203	3.91	7.60	405	3.935	7.80

Fig. 7.



It will be noticed that the first seven results show a slight rise of conductivity up to about 200° C. followed by a fall as the temperature was further raised to 390° C. This fall was evidently of a permanent nature as shown by the remaining results. These lie on a lower curve which becomes a straight line above 270° C. From that temperature up to 600° C.,  $K$  is independent of  $\theta$ . The last low temperature determination lies somewhat below the curve, indicating further permanent lowering of  $K$ .

These results resemble the first results obtained with the previous basalt cylinder in showing a slight initial rise of



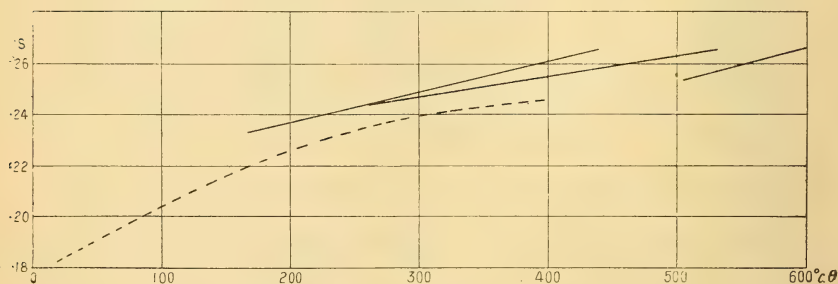
conductivity with temperature, but differ from them by about 20 per cent. in value. They differ entirely from the later results of the first experiment on basalt which showed a fall of conductivity with rise of temperature, and also from all the granite results. Accordingly another method was made use of to directly compare the conductivities of granite and basalt, and ascertain whether there is any large variation in their ratio with rise of temperature. These experiments, which will be described later, fully confirmed the results just given.

### *Specific Heat of Basalt.*

The method employed was the same as before. As the central aperture was only slightly larger than the wire, no correction for it was necessary. The results of one rising and three falling temperature determinations are plotted in fig. 8. The mean result for the specific heat is

$$S = 0.188 + 0.265 \times 10^{-3}\theta - 0.25 \times 10^{-6}\theta^2.$$

Fig. 8.



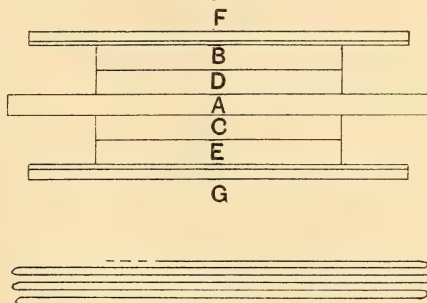
This gives a value 0.202 at 55° C. Dr. Joly's value for basalt between 10° and 100° is 0.19961, so that the agreement here is quite satisfactory.

### *Experiments on the Relative Conductivities of Granite and Basalt.*

The arrangement shown in fig. 9 was employed to compare the conductivities of the two rocks. A is a disk-shaped electric heater designed to generate heat uniformly over its surface. B and C are disks of granite, D and E disks of basalt. The diameter of these disks was 6.5 cm., their mean thickness, which was carefully measured, varied from 0.651 cm. to 0.715 cm., the granite disks being slightly thicker than the basalt ones. F and G are stout copper

disks separated from the rock disks by thin sheets of asbestos, cemented to the copper as shown. The whole was placed in the centre of a round metal vessel, 40 cm. in diameter by

Fig. 9.



12 cm. deep, filled with quartz sand. In these circumstances the flow of heat through the rocks would be almost uniform and perpendicular to the plane faces of the disks especially in the central parts, so the conductivities could be found if the temperatures of the rock-faces were known and the heat flux per square centimetre.

The temperatures were measured by means of thermocouples composed of the same wires as before used. One couple measured the sum of the two temperature differences across the two granite disks and another the sum for the two basalt disks, so that even if the heat flux upward were not quite equal to the flux downward, the conductivities could be found since the sum of the two fluxes was known. As the couple wires were only 0.1 mm. in diameter and the junctions were flattened to the same thickness, the couples were placed between the rock-faces, which were ground plane, without any grooves, and all the disks and the heater cemented together, the junctions being thus kept tight against their faces. It was hoped that in this way the well-known difficulty of ascertaining the temperature of a face across which heat is flowing would be overcome, and that the error caused by the layer of cement in which the couples were situated would be negligible, as this layer was only about 0.1 mm. thick.

The heating element was made of nichrome ribbon, 3.2 mm. wide by 0.55 mm. thick, wound zigzag as shown in the lower part of the figure. The successive parallel strips of the heater were separated by asbestos card, about 1 mm. thick, the whole being cemented together with cæmentium. Sheets of asbestos millboard 1.5 mm. thick were cemented over the two faces of the disk; the surfaces were thinly

coated with cement and ground plane. As the total width of one strip and insulation was 1.57 mm., the resistance per metre of the ribbon was 0.6493 ohm, and the total resistance of the heater at the same temperature was 3.68 ohms., we readily find that the energy developed per square centimetre was 1.122 per cent. of the total energy. As the temperature coefficient of nichrome is very small, errors due to the small inequalities of temperature of the ribbon towards the edges of the disk would be unimportant.

In order to avoid trouble with leakage into the couples alternating current was used. The energy was measured on a wattmeter of the Siemens dynamometer type, which as before controlled the relay for maintaining a constant energy supply. This instrument was carefully standardized on continuous current before use.

The initial determination at about 124° C. gave  $4.67 \times 10^{-3}$  and  $3.54 \times 10^{-3}$  as the conductivities of granite and basalt respectively. These results are some 12 to 15 per cent. lower than the corresponding results by the other method, but very approximately in the same ratio. There can be little doubt that the low values are due to the films of cement across which the heat-flow takes place. In the previous method the flow was parallel to the cement film in all cases.

Later results at higher temperatures apparently indicated a fall of conductivity of both rocks, that for the granite being much the larger. The results were rather inconsistent and the last results at 115° C. were actually much lower than those at 460° C. which immediately preceded them. This was almost certainly due to the failure of the cement, as on examination it was found to have given way between the rock disks. This failure must have been caused by differential expansion, as in other parts the cement was apparently unaffected by the heat. As cracking had probably started in the cement some time before the final rupture, the results are of little value, but indicate as far as they go that the conductivity of granite is about 35 per cent. higher than that of basalt at 124° C. before heating to higher temperatures, and falls much more rapidly as the temperature is raised.

As there seemed to be little chance of finding any cement which would withstand the stresses set up by differential expansion, the rock disks were ground together with carborundum powder until they fitted extremely closely and very fine grooves were cut in the outer faces of the inner rock disks to accommodate the couples measuring the temperatures of the faces between the rock disks, so that the rocks could

be fitted accurately together without any cement. These grooves were only just large enough to take the wires, small enlargements being made in the centre in which the junctions just fitted. As one groove was cut in a basalt disk and the other in a granite one and their depth was only about 0.1 mm., no allowance was made for them. No cement was used in putting the whole together, the asbestos on the heater and on the copper disks being wetted, and all the disks being pressed into close contact with each other by means of a 5 kilogram weight. The lower copper disk was supported inside the sand vessel by a glass ink-jar and a similar one inverted over the upper copper disk carried the weight, which thus was not in close thermal contact with the disks.

The results are shown in Table VI. in which  $K_1$  and  $K_2$  are the conductivities of granite and basalt respectively.

TABLE VI.

$\theta$ .	$K_1$ .	$K_2$ .	$\frac{K_1}{K_2}$ .
47° C.	$2.64 \times 10^{-3}$	$2.07 \times 10^{-3}$	1.275
108	2.67	2.13	1.255
163	2.63	2.17	1.21
213	2.76	2.38	1.16
355	2.68	2.52	1.065
517	2.80	2.75	1.02

It is evident that these values are much too low. This is almost certainly due to the thermal resistance of the various minute air-films which must occur in spite of the attempts to reduce them. These minute crevices exist not only between the rock disks but also between the inner and outer junctions and the faces whose temperatures they are supposed to measure. Their effect will probably vary with the temperature and, as it is quite probable that radiation plays an important part in the transference of heat across them, their thermal resistance probably decreases as the temperature is raised. Hence the method is not suited for measuring either the absolute value of the conductivity of a rock or its variation with temperature, but there seems to be no reason to doubt its evidence that basalt is a considerably worse conductor than granite at low temperatures, and that the



conductivities become nearly equal at about  $500^{\circ}\text{C}$ . This agrees well with the results obtained in the second basalt determination of the cylinder method.

### *Conclusion.*

There seems to be little doubt that the conductivity of granite falls from nearly  $6 \times 10^{-3}$  to under  $4 \times 10^{-3}$  as the temperature is raised to  $500^{\circ}\text{C}$ ., the conductivity rising again to about  $4.7 \times 10^{-3}$  on cooling.

As regards basalt, the second series of determinations was so much more satisfactory than the first, with regard to both the conditions of the experiment and the consistency of the results, that there seems to be little reason to question it, especially as the value obtained in it for the specific heat agrees so well with the known value at low temperatures. Further evidence of the different effect of rise of temperature on the two rocks is given by the disk experiment, which supports the later results. According to these the conductivity of basalt rises slightly with the temperature up to about  $270^{\circ}\text{C}$ ., above which it is constant and nearly equal to  $4 \times 10^{-3}$  up to  $600^{\circ}\text{C}$ . There is also, however, a small initial permanent lowering of conductivity caused by heating the rock.

This difference in the behaviour of the two rocks may possibly be explained as follows :—The lowering of the conductivity of granite is chiefly, or perhaps entirely, due to the formation of very minute cracks caused by the unequal expansion of the different mineral constituents. These cracks, which are formed as the rock is being heated, will naturally tend to close up again as the rock cools, thus causing a partial recovery of conductivity. Basalt, on the other hand, being much finer grained does not show this effect to nearly the same extent, though the small permanent fall of conductivity noticed is probably due to the same cause. The small rise of conductivity caused by heating basalt to about  $250^{\circ}\text{C}$ . may be due to another much coarser system of cracks, which were actually visible as very fine lines on the surfaces of all the specimens of basalt used. These cracks were almost certainly formed during the original cooling and contraction of the rock, and hence would partially close when the rock was expanded by heat, thus raising the conductivity. These coarser cracks were not noticed in the granite specimens, probably owing to the different mode of formation of that rock. Their absence probably explains why the low temperature conductivity of

granite is so much greater than that of basalt. It is just possible that frequent heating and cooling of some specimens of basalt might cause the development of the more minute system of cracks to such an extent as to cause a considerable permanent lowering of the conductivity accompanied by a change in the effect produced by heating, so that the conductivity would fall like that of granite. This is just what was noticed in the first basalt determinations. but these, as has been shown, were not of a sufficiently reliable nature for much stress to be laid on their results.

It would seem as a result of all the determinations that for temperatures up to  $500^{\circ}$  or  $600^{\circ}$  C. the conductivity of the earth's crust may be taken as about  $4 \times 10^{-3}$  without risk of serious error, unless the conductivity is sensibly affected by the large pressures involved.

In conclusion I wish to express my sincere gratitude to Dr. Joly for his kind interest and many valuable suggestions during the progress of the work.

Physical Laboratory,  
Trinity College, Dublin,  
October 6th, 1913.

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VI. *Delta Rays from Gases.*  
By NORMAN CAMPBELL, *Sc.D.\**

1. **I**T is generally believed that when the molecules of a gas are ionized the electrons are expelled from them with velocities similar to those of the  $\delta$  rays from metals; the belief is based upon the exact parallelism of the ionizing powers of rays and their power of exciting  $\delta$  rays from metals. There appears to be no direct experimental support for the belief, no observations on the ionization of gases which make it necessary to believe that the electrons ejected in ionization have an average initial velocity of several volts †. The absence of such observations appears to be due to the fact that measurements of the ionization of gases have been made at too great pressures or in too great electric fields.

\* Communicated by the Author.

† Kleeman (Proc. Roy. Soc. lxxxiii, p. 195 (1910)) produced evidence that the electrons liberated in ionization possess a finite average momentum in the direction of that of the ionizing rays; but, since it appears that the  $\delta$  rays from metals do not possess such a momentum, his experiments, whatever their interpretation, do not support the belief mentioned.

If the pressure is too great the electrons ejected in ionization lose their initial velocities by collision with the molecules before they can make their presence felt at the electrodes; if the electric field is too great their initial velocities are inappreciable compared with those that they acquire in moving under the field. Evidence for the existence of  $\delta$  rays in gases would be best obtained by studying the ionization of a gas at a very low pressure in a field such that the greatest difference of potential is not great compared with that of the initial velocity of the  $\delta$  rays.

2. Let us consider what should be the relation between  $i$ , the current through a gas contained in a parallel plate condenser, and  $V_0$ , the potential difference between the plates, when the pressure of the gas is so low that collisions between the electrons liberated and the molecules of the gas are negligibly rare. The current will consist of three parts. (1) There will be the current carried by the  $\delta$  rays from the electrodes. If the same number,  $N$ , of  $\delta$  rays are liberated from each electrode, and if  $f(V)$  is the fraction of these rays emitted in such a direction and with such a velocity that they cannot reach the opposite electrode against an opposing potential  $V$ , then this part of the current is  $Ne \cdot f(V_0)$ .  $N$  and  $f(V_0)$  can be determined by measurements when the pressure of the gas is zero\*. (2) There will be the current carried by the positive ions which are left when the molecules are ejected. The "initial velocity" of these positive ions, due to the reaction from the electrons ejected, will, if the velocity of those electrons is nearly the same as that of the  $\delta$  rays from metals, be less than 0.001 volt and small compared to their velocity of thermal agitation at room temperatures (0.033 volt). Since in the circumstances considered recombination will not occur, the number of these ions arriving at the oppositely charged electrode will be determined by their diffusion; this part of the current will be similar to that studied in a recent paper†. If  $n$  is the number of such ions formed per second this part of the current will be

$$ne(1 - 2\mu/V_0),$$

where  $\mu$  is about 0.025 volt at room temperatures. (3) There will be the current conveyed by the  $\delta$  rays from the gas.

\* Some of the  $\delta$  rays arriving at the electrodes are reflected there (*cf.* Phil. Mag. Aug. 1911, p. 276 and Jan. 1912, p. 46), but, if we may assume that reflexion affects the  $\delta$  rays from gases in the same way as those from metals, the following considerations are independent of the effects of reflexion.

† Phil. Mag. Nov. 1913, p. 912.

The total number of such rays produced is, of course, again  $n$ . If  $f'(V)$  is the fraction of these rays so emitted from the molecules that they cannot reach the negative electrode when the difference of potential between that electrode and the place where they are produced is  $V$ , then it is easy to show that this part of the current is

$$\frac{ne}{V_0} \int_0^{V_0} f'(V_0) dV.$$

Hence we shall have

$$i/e = Nf(V_0) + n(1 - 2\mu/V_0) + \frac{n}{V_0} \int_0^{V_0} f'(V) dV. \quad (1)$$

3. Now let us consider how this equation will be modified when the pressure of the gas is not so low that the effects of collisions between electrons and molecules are wholly negligible. Valuable information as to the results of such collisions is provided by the recent work of Franck and Hertz \*. They show that, when the gas is hydrogen or helium, the number of collisions made by an electron in travelling through the gas can be determined from the mean free path of an electron calculated from the data of the dynamical theory of gases; and also that, as a result of the collision, the electron is usually reflected with a very small loss of energy. Their experiments have not yet been extended to gases, such as oxygen, which possess a marked "affinity for electrons," but they think it probable that the number of collisions in this case is again calculable from the gas theory free path, while the electron is not reflected but adheres to the molecule with which it collides.

When an electron adheres to a molecule it becomes an ion very similar to the positive ions which carry the part of the current (2). In all the cases which we shall consider this part of the current is very nearly saturated, and hence we may suppose that every electron which adheres to a molecule arrives ultimately at the oppositely charged electrode, whether it would or would not have done so if the collision had not occurred. Assuming that the proportion of electrons which can travel a distance  $x$  without collision is  $e^{-x/\lambda}$ , where  $\lambda$  is the free path of an electron and is taken to be independent of its velocity within the limits considered, we find in place of (1)

$$i/e = N \left[ 1 - e^{-\frac{l}{\lambda}} \{ 1 - f(V_0) \} \right] + n(1 - 2\mu/V_0) + \frac{n}{V_0} \int_0^{V_0} \left[ 1 - e^{-\frac{lV}{\lambda V_0}} \{ 1 - f'(V) \} \right] dV \quad (2)$$

\* J. Franck & G. Hertz, *Deutsch. Phys. Ges.* xv. 9, p. 373 (1913).



It is to be observed that the effect of the collisions with the molecules of the gas is to increase both the first and the third terms on the right hand of the equation.

When the gas is one which has no affinity for electrons and reflects rather than absorbs them, the effect of collisions is somewhat different. It is now possible that a  $\delta$  ray starting from one electrode may be reflected back to that electrode; the number of such  $\delta$  rays crossing the condenser is diminished. Further, since there is little loss of energy at reflexion, and since the reflecting power of the molecules does not change rapidly with the speed of the electrons, the proportion of the electrons starting from one electrode which are deflected back to it will be nearly the same whether they are emitted with or against the field, so long as the potential difference between the electrodes is small compared with the velocity of emission. The collisions with the molecules will diminish the part of the current due to the  $\delta$  rays from the electrodes for such small potentials, while in the case of unelastic collision they increased it. On the other hand collisions, even if perfectly reflecting, will not diminish the current carried by the  $\delta$  rays from the gas, for these electrons must arrive ultimately at one of the two electrodes and cannot cease to act as carriers by being reflected to the place where they were generated. The current carried by these  $\delta$  rays depends on the ratio of those which arrive ultimately at the oppositely charged electrode to those which arrive at the similarly charged electrode; reflexion cannot decrease this ratio; it will increase it if there is any loss of energy at reflexion. Accordingly the third part of the current will be increased whether the collisions are elastic or unelastic, but to a greater extent in the second case.

The second part of the current is independent of the number of collisions, and in any case it is always very nearly saturated.

4. Let us now examine the experimental facts in the light of the foregoing discussion. Some apparently strange results of measurements of the current through ionized air and hydrogen at low pressure were described in a former paper\*; they are now set out rather more fully in Tables I. and II. The distance between the electrodes as well as the pressure of the gas was varied; both quantities are expressed by the ratio  $l/\lambda$ , where  $l$  is the distance between the electrodes and  $\lambda$  the calculated free path of an electron in the gas; this ratio is given in the top row. The second row gives the value of  $n/N$ .  $N_e$  is the saturation current at zero pressure;  $n$  cannot be found by direct measurements of the saturation

\* Phil. Mag. Oct. 1912, p. 527.

current at the low pressure, for at these pressures the current is never saturated; ionization by collision occurs before saturation. But if it be assumed that  $n$  is proportional to the pressure, its value for low pressures can be determined from observations at high pressures, when saturation is attainable. For the purposes of the tables  $n$  is calculated by means of this assumption. The remaining figures in the

TABLE I.—Hydrogen.

$l/\lambda$ .....	0	0.68	1.24	1.98	3.35	6.32	7.28	10.0	11.7	17.4	26.3	Calc.
$n/N$ .....	0	0.10	0.18	0.28	0.48	0.91	0.99	1.36	1.68	2.50	3.59	
$V_0=1...$	0.465	(-0.07)	0.28	0.37	0.50	0.65	0.64	0.74	0.79	0.83	0.93	0.59
2...	0.651	(-0.17)	0.09	0.28	0.42	0.62	0.60	0.71	0.76	0.82	0.93	0.69
3...	0.768	(-0.13)	0.16	0.25	0.36	0.59	0.58	0.69	0.74	0.81	0.91	0.74
5...	0.887	0.03	0.21	0.29	0.42	0.59	0.58	0.68	0.74	0.80	0.91	0.81
10...	0.980	0.51	0.55	0.61	0.57	0.67	0.65	0.74	0.78	0.83	0.93	0.89
20...	0.997	1.08	1.26	1.10	0.95	0.87	0.83	0.95	0.87	0.89	1.01	0.94
30...	1.000	1.74	1.77	1.63	1.34	1.08	1.04	0.99	0.96	0.93	1.07	0.95
50...	—	2.36	2.53	2.41	2.14	1.68	1.61	1.38	1.24	1.07	1.24	0.97

TABLE II.—Air.

$l/\lambda$ .....	0	0.35	0.76	1.43	2.34	2.76	3.63	4.60	7.75	10.0	Calc.
$n/N$ .....	0	0.10	0.24	0.42	0.71	0.82	1.16	1.39	2.48	3.00	
$V_0=1...$	0.465	0.40	0.60	0.62	0.57	0.60	0.56	0.58	0.61	0.66	0.59
2...	0.651	0.53	0.63	0.68	0.65	0.67	0.65	0.67	0.68	0.70	0.69
3...	0.768	0.56	0.64	0.68	0.70	0.67	0.69	0.70	0.72	0.71	0.74
5...	0.887	0.66	0.66	0.70	0.76	0.70	0.75	0.76	0.78	0.74	0.81
10...	0.980	0.83	0.75	0.78	0.82	0.78	0.84	0.84	0.86	0.81	0.89
20...	0.997	0.96	0.98	0.97	0.97	0.94	0.95	0.97	0.93	0.87	0.94
30...	1.000	1.04	1.19	1.16	1.18	1.15	1.12	1.14	1.01	0.84	0.95
50...	—	1.33	1.55	1.52	1.62	1.59	1.55	1.57	1.33	1.19	0.97

first column give the fraction of the total current\* at zero pressure carried by the  $\delta$  rays from the electrodes which is obtained with the potential difference in the corresponding row of the first column; they also give the values of  $f'(V)$

\* The  $\delta$ -ray current is taken to be saturated at 30 volts. It has been noted by several observers that at higher voltages the current decreases, and this decrease has been explained by Bumstead as due to the emission of  $\delta$  rays with much higher speeds which cause the emission of the low speed  $\delta$  rays. The high speed  $\delta$  rays are here left out of account, for though probably much of the ionization is really due to them, they are so few in number and have speeds so high compared to the potentials applied that they do not carry any appreciable portion of the current.

for those potentials. The other columns give the values of  $\frac{i_p - i_0}{ne}$  for the various potentials, where  $i_p$  is the measured current through the condenser at the pressure concerned,  $i_0$  that with the same potential at zero pressure. If (1) were applicable they would thus represent the part of the current due to the gas and would be equal to

$$1 - 2\mu/V_0 + \frac{1}{V_0} \int_0^{V_0} f'(V) dV.$$

The last column (marked *calc.*) gives the values of this expression on the assumption that the  $\delta$  rays from a layer of gas are emitted with the same speeds as those from the surface of a metal, so that  $j'(V) = f(V)$ . The integral is calculated by quadrature from the numbers in the first column. The probable error of the numbers in all the columns but the first is about 0.03. It is so large, firstly because the currents to be measured are small and the numbers recorded are only differences between measured currents; secondly, because the value of  $N$  is somewhat uncertain. As several observers have found,  $N$  depends in some measure on the gas film on the surface of the electrodes and may alter when the pressure is changed.

5. Let us first consider the results for hydrogen.

The measurements when  $V_0$  is 20 volts or more are clearly affected by ionization by collision and hence have no bearing on the present discussion. For the rest attention is directed to the following features: first, the numbers increase regularly with  $l/\lambda$ ; second, the numbers in each column do not increase regularly with  $V_0$  but have a minimum at about 3 volts; third, the numbers for small values of  $l/\lambda$  and  $V_0$  are very much less than those calculated from (1); they are often less than those corresponding to the second term in that equation which represents the current carried by the positive ions only; fourth, in the first columns there are negative numbers, that is to say, the presence of a little gas in the condenser actually diminishes the current flowing through it with small voltages\*.

It is clear that none of these features can be explained on the basis of (1); but they may be explained, at any rate partially, on the basis of the discussion of the effect of a small amount of hydrogen. We saw that the main effect of

\* The decrease is very small and on the margin of experimental error, but the experiment was repeated several times and always gave a decrease.

a little hydrogen was likely to be a decrease in the current carried by the  $\delta$  rays from the electrodes. The numbers given in the Table are obtained by subtracting from the measured current that carried by those rays in a vacuum ; if the rays carry less current when gas is present, the numbers in the Table will all be smaller than they would be if (1) were applicable. If, owing to the presence of gas, the current due to the  $\delta$  rays from the electrodes is decreased by more than the extra current due to the ionization of the gas, the negative figures in the first column would be explained. The minimum in any column at about 3 volts could be explained if the effect of the field in counteracting the effects of reflexion do not begin to be appreciable until  $V_0$  is greater than 3. Again, of course, on this view the observed numbers will all be less than those calculated, until the current carried by the  $\delta$  rays from the electrodes becomes inappreciable compared with that due to the gas. But when this stage is reached the effect of collisions in increasing the current due to the  $\delta$  rays from the gas is important, so that we immediately pass to the stage where the observed numbers are greater than the calculated. The data concerning the reflexion of the electrons by collision are not so definite that any attempt can be made to explain the results quantitatively ; and certainly it seems impossible to deduce from these results any conclusion concerning the initial velocity of the  $\delta$  rays from the gas.

6. Now let us turn to the results for air. Here again, the measurements when  $V_0$  is 30 volts or more are affected by ionization by collision. Again, also, there is a general increase in the numbers in each row with  $l/\lambda$ , but the increase is not nearly so marked as before ; the numbers are approximately constant between  $l/\lambda=1$  and  $l/\lambda=4$ , and in this range they show some approximation to those calculated from (1). The numbers in each column increase regularly with  $V_0$ , but the rate of increase is small in the region where in the previous case there was a minimum.

In interpreting these results we must remember that, of the two gases in air, nitrogen has no affinity for electrons \* and probably acts like hydrogen, while oxygen has a strong affinity. Accordingly the nitrogen will tend to decrease the current carried by the  $\delta$  rays from the electrodes, and so make the numbers smaller than those predicted by (1), while the oxygen tends to increase both this current and that due to the  $\delta$  rays from the gas, and so make the numbers too

\* See the measurements on the velocities of the ions by Franck, *Deutsch. Phys. Gesell.* xii. p. 613 (1910).



large. It is possible, accordingly, that the smallness of the numbers for  $l/\lambda=0.35$  is due to the preponderant action of the nitrogen, while the constancy of the numbers for somewhat greater values of  $l/\lambda$  is due to the compensating action of the two gases. At any rate, the difference between the results for hydrogen and air, the fact that the numbers are almost uniformly greater in the case of air for the same value of  $V_0$  and  $l/\lambda$ , is exactly what would be expected to be the result of the presence of a strongly electronegative gas.

But the main interest of the experiments lies in the question whether they can give any information as to the initial velocity of the  $\delta$  rays from gases. It appears necessary to suppose that these  $\delta$  rays have a finite initial velocity, and that it is of the same order of magnitude as that of the  $\delta$  rays from metals. No other explanation can, I think, be given of the fact that in no case is the current through the gas saturated when  $V_0=20$ , even though the currents due to the  $\delta$  rays from the electrodes and that due to the positive ions is saturated with that potential. If the constancy of the numbers in the Table over a certain range of  $l/\lambda$  means that within this range (1) is applicable, we should have to conclude that the  $\delta$  rays from the gas are, on the average, a little faster than those from the electrodes, since the numbers in the Table are a little smaller than those calculated on the assumption that  $f(V)=f'(V)$ .

However, it does not appear that this method is capable of giving any very precise indications concerning the properties of these rays. They do appear to show that it is necessary to suppose that the rays have a finite initial velocity, and so provide evidence for an important proposition which was universally accepted but had never been directly proved. But this discussion has been published mainly because a brief account of the measurements had been given without any attempt at an explanation of them. It seems that they are generally in accordance with the recent addition to our knowledge of the interaction between electrons and molecules.

#### SUMMARY.

The theory is considered of the conduction through an ionized gas when the pressure of the gas is so low that the free path of an electron is not small compared with the distance between the electrodes, and the number of ions made in the gas is not large compared with the number of  $\delta$  rays made at the electrodes. The discussion is based

mainly on the recent work of Franck and Hertz on the collisions between electrons and atoms.

The results of some measurements published previously are considered in the light of the theory. They seem in general accordance with that work. They cannot be explained quantitatively at present, but it appears that they make it necessary to believe that  $\delta$  rays are emitted from ionized molecules of gases with velocities of the same order of magnitude as those from metals.

Leeds University,  
August 1913.

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## VII. *An Experiment on Rotatory Polarization in Liquids.*

*By* E. TALBOT PARIS and ALFRED W. PORTER, *F.R.S.\**

THE experiment recorded here was carried out in order to see if any evidence could be obtained of a directive action on the molecules of an optically active substance in solution by light passing through the solution. If such a directive action existed (the light tending to orientate the molecules in a certain direction relative to its direction of propagation), it would be expected that when light first passes into the liquid a small interval of time would be required for the full rotatory power to be developed. In this case, if an intermittent source of light were used, giving flashes of sufficiently short duration, the rotation of the plane of polarization would be less than that for a steady source. In the experiment described below the rotation produced in a long tube of cane-sugar solution was measured, first using a steady source of light (a mercury lamp), and afterwards an intermittent one in the form of a platinum-mercury spark.

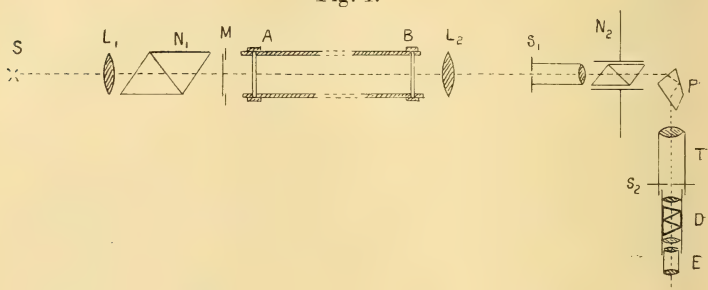
The arrangement of the apparatus is shown in fig. 1.

Light from the source S (the mercury arc or spark as the case may be) passes through the collimating lens  $L_1$  and the polarizing nicol  $N_1$ . Sensitiveness is obtained by means of a half-wave plate of mica at M, placed across the middle of the field so as to give a "three-field" arrangement. The sensitiveness can be altered by rotating  $N_1$ . The sugar solution was contained in a long iron tube AB, fitted with plate-glass ends. To prevent the solution becoming contaminated with the iron, this tube was galvanized; the inside was painted with photographic black to avoid reflexions. The length of the solution in the tube was about 165 cm., and the rotation for the green mercury line

\* Communicated by the Authors.

( $\lambda 5461$ ) was  $534.3$  degrees. To obtain a sufficiently clear solution it was necessary to mix some freshly precipitated and washed aluminium hydroxide with it and filter the liquid warm. This removes practically all suspended matter.

Fig. 1.



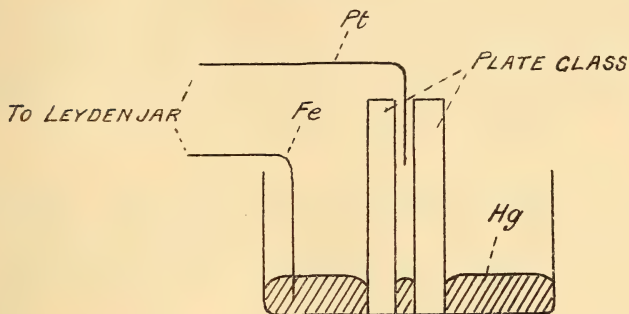
The lens  $L_2$  forms a reduced image of the half-wave plate,  $M$ , on the slit  $s_1$ . The remainder of the apparatus, comprising the analysing nicol  $N_2$ , the constant-deviation prism  $P$ , and the telescope  $T$ , was adapted from a spectrophotometer. The graduated circle attached to  $N_2$  was fitted with a vernier attachment reading to minutes. Light of the required wave-length is sorted out by rotating the prism  $P$  and adjusting the slit  $s_2$ . The telescope is focussed on the slit  $s_1$  so that a sharp image of the half-wave plate is seen.

All measurements were made with the green mercury line ( $\lambda 5461$ ). Further purification of the light after its passage through  $P$  was found necessary, and so the direct-vision spectroscope  $D$  was inserted between the eyepiece  $E$  and the rest of the telescope. With the light from the arc there was some diffuse light from the yellow mercury lines present, and with the spark, in addition to the diffuse yellow light, some green light on each side of the mercury line, but less intense. This green light was not diffuse but formed a definite image of the half-wave plate.

The spark was produced by the discharge of a large leyden-jar connected with an induction-coil, and passed between a platinum wire and a layer of mercury at the bottom of a glass vessel, contact with the mercury being made with a piece of iron wire soldered on to the end of the lead from the leyden-jar. Considerable inconvenience in taking the readings was caused by the irregular movements of the spark, a small change in its position causing the image formed by the lens  $L_2$  to move off the slit  $s_1$ . To keep the spark as much as possible in one position the platinum wire was placed between two pieces of plate-glass standing about

2 mm. apart in the mercury (see fig. 2). The spark gap was about 1 cm.

Fig. 2.



To determine approximately the duration of the spark, photographs were taken of tinned iron wires threaded radially near the rim of a rotating wooden disk, the disk itself being painted black. The disk was driven by a small motor to which was attached a revolution-counter. The following times were observed during which the disk made 500 revolutions:—15·0, 15·4, 14·8, 15·4, and 14·8 secs., giving a mean of 15·1 secs., or 2000 revns. per minute very nearly. The middle points of the wires, each about a centimetre long, were 19 cm. from the centre of the disk. A camera was focussed on the wires so as to give a magnification of 2, and the disk having been set rotating, photographs were taken by the light from the spark. The velocity of the wires being 3980 centimetres per second, a blur of width  $x$  cm. on the photograph will be produced by a spark of duration  $t$  secs. where

$$x = 2 \times 3980 t.$$

If the duration of the spark were  $3 \times 10^{-6}$  sec. the blur in the photographs would be ·24 mm. A number of photographs were taken of the moving wires and compared with photographs taken under similar conditions but with the wires at rest. No blur, however, could be detected; therefore the duration of the spark probably does not exceed 3 millionths of a second.

Owing to the intermittent nature of the light from the spark, it was not possible to use the most sensitive arrangement of the apparatus. A half-shade angle of about 12° to 20° was necessary. The reading for the arc was first taken and then the spark substituted for the arc and a fresh observation made. The temperature of the solution was



indicated by two thermometers passing through side-tubes—one at each end of the tube containing the solution. The temperature of the solution in all the experiments was about  $18^{\circ}\text{C}$ . It must be pointed out that large readings mean *small* rotation. The position of the *polarizer* is different for each set of readings, so that there is no relation between the numbers in different sets. This of course does not interfere with a comparison of the arc and spark readings.

Set.	Circle-reading for arc- light.	Circle-reading for spark- light.	Set.	Circle-reading for arc- light.	Circle-reading for spark- light.
I.	96° 59'	96° 56'	II.	97° 33'	97° 26'
	54	53		27	15
	56	0		25	23
	57	4		30	32
	57	2		33	36
		96 57			29
		97 1			23
		96 57 48			
III.	100° 32'	100° 24'	IV.	97° 22'	97° 36'
	30	42		25	9
	34	21		25	32
	33	23		27	26
	35	34		27	23
	30	21		25	20
	34	42		27	53
	33	47		26	15
	31	46		25	30
	33	47		25	29
				27	36
					38

If all the observations are included in the estimate of the means, the values are as follows :—

	<i>Arc.</i>		<i>Spark.</i>	
Set I. ....	96°	56'·6	96°	57'·5
II. ....	97	29·6	97	26·3
III. ....	100	32·5	100	34·7
IV. ....	97	25·5	97	28·9
Grand means ...	98	36·05	98	36·8

The total rotation is about  $500^{\circ}$ ; hence the grand means differ by less than 1 minute in  $500^{\circ}$ , or less than 1 part in 30,000. It is noteworthy, however, that in three out of the four sets the rotation is less for the spark than for the arc. In the exceptional set (II, spark) occurs one very low reading—too low to be due to ordinary experimental errors.

If this reading were excluded there is a difference in the grand means of about one part in 13,000—the rotation in the case of the spark being the less. Since this is within the possible error of the experiment, the final result may be stated by saying that so far as these experiments go there is no certain indication of a directive action of light upon the molecules of the sugar in solution.

University College,  
London.

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VIII. *On the Viscosity of Calcium Chloride Solutions.* By  
FREDERICK SIMEON, *B.Sc., Physics Research Scholar, University of London, University College* \*.

WHILE the present work was in progress, an account of work on the same subject was read before the Physical Society of London by Mr. Tucker †. However, so much of the present work had been done, and the apparatus in use differed in so many respects from that used by Mr. Tucker, that it seemed well to proceed until a comparison of results could be made.

The apparatus employed was identical in principle with that used by Thorpe and Rodger ‡. It consisted of a horizontal capillary tube, about 30 cm. long and 0.4 mm. in diam., connected to two vertical tubes about 18 cm. long and 1 sq. cm. cross-section. A fixed quantity of the liquid whose viscosity was to be determined was forced through the capillary tube under constant pressure from one upright tube to the other, and the time of passage carefully observed. The apparatus was immersed in a large bath of water at constant temperature until the lines on the upright tubes which determined the volume of liquid transmitted were just visible above the edge of the bath.

At least six, and usually eight to twelve readings of the time of passage, which did not vary by more than about 0.2 per cent., were made for each solution.

The coefficient of viscosity is calculated from the ratio of this time to the corresponding time for pure water, assuming the values for water found by Thorpe and Rodger. The times of passage in opposite directions differ by a very small amount due to slight asymmetry in the apparatus; but, in practice, the times in opposite directions were kept separate, and thus two values for the ratio of viscosities were found which agreed very closely.

\* Communicated by Prof. A. W. Porter, F.R.S.

† Proc. Phys. Soc. vol. xxv. p. 111.

‡ Phil. Trans. 1894, A. p. 1.

*Theory.*—For the flow of liquid through a horizontal tube we have Poiseuille's equation

$$\eta = \frac{(p_1 - p_2)\pi t}{8lQ} \cdot r^4,$$

where  $\eta$  = coefficient of viscosity of liquid,  
 $p_1 - p_2$  = driving pressure,  
 $Q$  = quantity transmitted in time  $t$ ,  
 $r$  = radius of tube,  
 and  $l$  = length of tube.

In the experimental arrangement there is a constant driving pressure  $\Pi$ , and a variable pressure due to the difference in level of the liquid in the vertical tubes. The resultant pressure varies from  $(\Pi + \rho gh)$  to  $(\Pi - \rho gh)$  during a reading, where  $\rho$  = density of liquid, and  $h$  = change of level in either tube. The average pressure is  $\Pi$ , but there is a small influence of the variation of pressure which can be calculated.

On integration, the expression for  $\eta$  becomes

$$\eta = k \cdot t \cdot \frac{\rho}{\log \frac{\Pi + \rho gh}{\Pi - \rho gh}},$$

where  $k = \frac{g\pi r^4}{4Al}$  = const. for the particular apparatus,  $A$  being the area of cross-section of each vertical tube.

There is another constant of the apparatus, viz.  $\frac{gh}{\Pi} = \alpha$  (say), and so

$$\eta = k \cdot t \cdot \frac{\rho}{\log \frac{1 + \alpha\rho}{1 - \alpha\rho}}.$$

If the suffixes  $s$  and  $w$  denote values for solution and water respectively, we have

$$\frac{\eta_s}{\eta_w} = \frac{t_s}{t_w} \cdot \frac{\rho_s}{\rho_w} \cdot \frac{\log(1 + \alpha\rho_w) - \log(1 - \alpha\rho_w)}{\log(1 + \alpha\rho_s) - \log(1 - \alpha\rho_s)}.$$

As a test of the accuracy of the method, the average times of passage of distilled water at  $15^\circ \text{C.}$  and at  $20^\circ \text{C.}$  were found. Assuming Thorpe and Rodger's value at  $15^\circ \text{C.}$ , the value at  $20^\circ \text{C.}$  was calculated from the ratio of these times, and it was found to differ from their value at  $20^\circ \text{C.}$  by not more than  $\frac{1}{10}$  per cent.

A series of measurements of the viscosities of calcium-chloride solutions of varying concentrations up to saturation was made at  $15^\circ \text{C.}$  The following results were obtained.

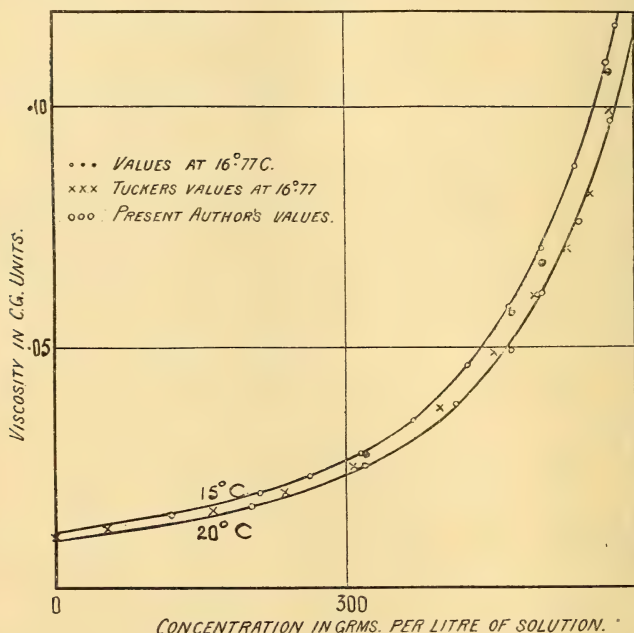
TABLE I.

15° C.                      20° C.                      16°·77 C.                      Tucker's Values, 16°·77 C.

Density.	Concentration in gms. of $\text{CaCl}_2$ per litre of solution.	Viscosity in c.g.s. units.	Density.	Concentration in gms. of $\text{CaCl}_2$ per litre of solution.	Viscosity in c.g.s. units.	Density.	Concentration in gms. of $\text{CaCl}_2$ per litre of solution.	Viscosity in c.g.s. units.
1	0	·011336	1	0	·00974*	·9988	0	·01081
1·097	123·5	·01528	1·157	204·2	·01704	1·0434	56·36	·0121
1·163	213·5	·01980	1·239	321·3	·02542	1·1293	163·95	·0161
1·199	263·5	·02324	1·301	415·9	·03817	1·1793	238·05	·0199
1·236	318	·02795	1·341	473·4	·04946	1·2313	308·87	·0251
1·271	371	·03468	1·358	504·2	·06143	1·2933	399·35	·0371
1·308	427·8	·04604	1·382	542·5	·07603	1·3308	454·80	0486
1·336	470	·05861	1·404	575	·09733	1·3569	496·32	·0602
1·358	504·2	·07089	* Thorpe and Rodger give $\eta_{20} = 0·009983$ .					·0706
1·380	538·2	·08756						·0818
1·401	572·2	·10945						·0989
1·411	580	·11709						·3320



The curve connecting concentration and viscosity was found to be not parallel to the corresponding curve of Tucker's values at  $16^{\circ}77$  C., as had been expected, and so another series of measurements was made at  $20^{\circ}$  C. in order



to determine the temperature coefficient for a small range, viz.  $5^{\circ}$  C. The curve drawn from the last set of numbers is parallel to that for  $15^{\circ}$  C, and cuts the curve of Tucker's values at a high concentration. A few determinations made at  $16^{\circ}77$  C., however, seem to indicate that with the apparatus used another parallel curve would be obtained at that temperature.

An important difference between the two forms of apparatus is the length of the capillary tube. The formula employed to calculate the viscosity in either case takes no account of the end effect, but applies rigorously only in the case where the stream-lines are parallel to the walls of the tube. For a long tube, therefore, the ratio of the amount of viscous work done at the ends of the tube where the stream-lines are not parallel to that done in passing along the tube will be much less than is the case for a short tube, and the unknown error arising from this will be more nearly negligible. It will be noticed that the tube used in these

TABLE II.—Table of Values of Densities at various concentrations.  $\text{CaCl}_2$  solution.

Gerlach (15° C.)*.		Schiff (18°·3 C.)*.		Kohlrausch (18° C.)*.		Pickering (17°·9 C.)†.		Tucker (16°·77 C.).		Simeon (16° C.). Experimental values.	
Density.	Concentration.	Density.	Concentration.	Density.	Concentration.	Density.	Concentration.	Density.	Concentration.	Density.	Concentration.
1·04259	52·1	1·0407	53·1	1·0409	52	1·041	52	1·0434	56·36	1·1558	204·16
1·08695	108·7	1·0838	109·8	1·0852	108·5	1·094	120·4	1·1293	163·95	1·2413	325·30
1·13360	170	1·1292	171·6	1·1311	169·7	1·131	169·6	1·1793	238·05	1·3054	422·73
1·18222	236·3	1·1768	238·3	1·1794	236	1·189	248	1·2313	308·87	1·3584	504·21
1·23365	308·2	1·2262	310·8	1·2305	308	1·250	337·5	1·2933	399·35	1·3805	538·17
1·28789	386	1·2773	388·5	1·2841	385·5	1·338	468·5	1·3308	454·80	1·4014	572·22
1·34430	470·5	1·3300	472	1·3420	469·5	1·406	576	1·3569	496·32		
1·40330	561			1·400	560	1·429	614	1·3788	529·13		
								1·3960	553		
								1·4068	574·96		

\* Quoted in Castell-Evan's Physico-Chemical Tables.

† Quoted in Kaye & Laby's Table of Physical Constants.

determinations was 15 times as long as that used by Mr. Tucker.

Most of the determinations were made with solutions made up from "pure fused" calcium chloride, but determinations made with solutions made up from "pure crystals" gave identical results. The densities recorded in Table II. were made from the latter solutions. In the same table are recorded the values of the densities obtained by previous observers.

In conclusion, I should like to express my obligation to Prof. Porter for his kindness in guiding and encouraging me throughout this work.

IX. *Further Applications of Bessel's Functions of high order to the Whispering Gallery and allied Problems.* By Lord RAYLEIGH, O.M., F.R.S.\*

IN the problem of the Whispering Gallery† waves in two dimensions, of length small in comparison with the circumference, were shown to run round the concave side of a wall with but little tendency to spread themselves inwards. The wall was supposed to be perfectly reflecting for all kinds of waves. But the question presents itself whether the sensibly perfect reflexion postulated may not be attained on the principle of so-called "total reflexion," the wall being merely the transition between two uniform media of which the outer is the less refracting. It is not to be expected that absolutely no energy should penetrate and ultimately escape to an infinite distance. The analogy is rather with the problem treated by Stokes‡ of the communication of vibrations from a vibrating solid, such as a bell or wire, to a surrounding gas, when the wave-length in the gas is somewhat large compared with the dimensions of the vibrating segments. The energy radiated to a distance may then be extremely small, though not mathematically evanescent.

\* Communicated by the Author.

† Phil. Mag. vol. xx. p. 1001 (1910); Scientific Papers, v. p. 619. But the numbers there given require some correction owing to a slip in Nicholson's paper from which they were derived, as was first pointed out to me by Prof. Macdonald. Nicholson's table should be interpreted as relating to the values, not of  $2 \cdot 1123 (n-z)/z^{\frac{1}{2}}$ , but of  $1 \cdot 3447 (n-z)/z^{\frac{1}{2}}$ , see Nicholson, Phil. Mag. xxv. p. 200 (1913). Accordingly, in my equation (5)  $1 \cdot 1814 n^{\frac{1}{2}}$  should read  $1 \cdot 8558 n^{\frac{1}{2}}$ , and in equation (8)  $51342 n^{\frac{1}{2}}$  should read  $8065 n^{\frac{1}{2}}$ .

‡ Phil. Trans. 1868. See 'Theory of Sound,' § 324.

A comparison with the simple case where the surface of the vibrating body is *plane* ( $x=0$ ) is interesting, especially as showing how the partial escape of energy is connected with the curvature of the surface. If  $V$  be the velocity of propagation, and  $2\pi/k$  the wave-length of plane waves of the given period, the time-factor is  $e^{ikVt}$ , and the equation for the velocity-potential in two dimensions is

$$\frac{d^2\phi}{dx^2} + \frac{d^2\phi}{dy^2} + k^2\phi = 0. \quad . \quad . \quad . \quad . \quad (1)$$

If  $\phi$  be also proportional to  $\cos my$ , (1) reduces to

$$\frac{d^2\phi}{dx^2} + (k^2 - m^2)\phi = 0, \quad . \quad . \quad . \quad . \quad (2)$$

of which the solution changes its form when  $m$  passes through the value  $k$ . For our purpose  $m$  is to be supposed greater than  $k$ , viz. the wave-length of plane waves is to be greater than the linear period along  $y$ . That solution of (1) on the positive side which does not become infinite with  $x$  is proportional to  $e^{-x\sqrt{(m^2-k^2)}}$ , so that we may take

$$\phi = \cos kVt \cdot \cos my \cdot e^{-x\sqrt{(m^2-k^2)}}. \quad . \quad . \quad (3)$$

However the vibration may be generated at  $x=0$ , provided only that the linear period along  $y$  be that assigned, it is limited to relatively small values of  $x$  and, since no energy can escape, no work is done on the whole at  $x=0$ . And this is true by however little  $m$  may exceed  $k$ .

The reason of the difference which ensues when the vibrating surface is curved is now easily seen. Suppose, for example, that in two dimensions  $\phi$  is proportional to  $\cos n\theta$ , where  $\theta$  is a vectorial angle. Near the surface of a cylindrical vibrator the conditions may be such that (3) is approximately applicable, and  $\phi$  rapidly diminishes as we go outwards. But when we reach a radius vector  $r$  which is sensibly different from the initial one, the conditions may change. In effect the linear dimension of the vibrating compartment increases proportionally to  $r$ , and ultimately the equation (2) changes its form and  $\phi$  oscillates, instead of continuing an exponential decrease. Some energy always escapes, but the amount must be very small if there is a sufficient margin to begin with between  $m$  and  $k$ .

It may be well before proceeding further to follow a little more closely what happens when there is a transition at a plane surface  $x=0$  from a more to a less refractive medium. The problem is that of total reflexion when the incidence is



grazing, in which case the usual formulæ\* become nugatory. It will be convenient to fix ideas upon the case of sonorous waves, but the results are of wider application. The general differential equation is of the form

$$\frac{d^2\phi}{dt^2} = V^2 \left( \frac{d^2\phi}{dx^2} + \frac{d^2\phi}{dy^2} \right), \dots \dots \dots (4)$$

which we will suppose to be adapted to the region where  $x$  is negative. On the right ( $x$  positive)  $V$  is to be replaced by  $V_1$ , where  $V_1 > V$ , and  $\phi$  by  $\phi_1$ . In optical notation  $V_1/V = \mu$ , where  $\mu$  (greater than unity) is the refractive index. We suppose  $\phi$  and  $\phi_1$  to be proportional to  $e^{i(by+ct)}$ ,  $b$  and  $c$  being the same in both media. Further, on the left we suppose  $b$  and  $c$  to be related as they would be for simple plane waves propagated parallel to  $y$ . Thus (4) becomes, with omission of  $e^{i(by+ct)}$ ,

$$\frac{d^2\phi}{dx^2} = 0, \quad \frac{d^2\phi_1}{dx^2} = b^2(\mu^2 - 1)/\mu^2, \quad \dots \dots \dots (5)$$

of which the solutions are

$$\phi = A + Bx, \quad \phi_1 = C e^{-bx\sqrt{(\mu^2-1)/\mu}}, \quad \dots \dots \dots (6)$$

$A, B, C$  denoting constants so far arbitrary. The boundary conditions require that when  $x=0$ ,  $d\phi/dx = d\phi_1/dx$  and that  $\rho\phi = \rho_1\phi_1$ ,  $\rho, \rho_1$  being the densities. Hence discarding the imaginary part, and taking  $A=1$ , we get finally

$$\phi = \left\{ 1 - \frac{\rho bx\sqrt{(\mu^2-1)}}{\rho_1\mu} \right\} \cos(by+ct), \quad \dots \dots \dots (7)$$

$$\phi_1 = \frac{\rho}{\rho_1} e^{-bx\sqrt{(\mu^2-1)/\mu}} \cos(by+ct). \quad \dots \dots \dots (8)$$

It appears that while nothing can escape on the positive side, the amplitude on the negative side increases rapidly as we pass away from the surface of transition.

If  $\mu < 1$ , a wave of the ordinary kind is propagated into the second medium, and energy is conveyed away.

In proceeding to consider the effect of curvature it will be convenient to begin with Stokes's problem, taking advantage of formulæ relating to Bessel's and allied functions of high order developed by Lorenz, Nicholson, and Macdonald†. The motion is supposed to take place in two dimensions, and ideas may be fixed upon the case of aerial

\* See for example 'Theory of Sound,' vol. ii. § 270.

† Compare also Debye, Math. Ann. vol. lxxvii. (1909).

vibrations. The velocity-potential  $\phi$  is expressed by means of polar coordinates  $r, \theta$ , and will be assumed to be proportional to  $\cos n\theta$ , attention being concentrated upon the case where  $n$  is a large integer. The problem is to determine the motion at a distance due to the normal vibration of a cylindrical surface at  $r=a$ , and it turns upon the character of the function of  $r$  which represents a disturbance propagated outwards. If  $D_n(kr)$  denote this function, we have

$$\phi = e^{ikvt} \cos n\theta \cdot D_n(kr), \quad (9)$$

and  $D_n(z)$  satisfies Bessel's equation

$$D_n'' + \frac{1}{z} D_n' + \left(1 - \frac{n^2}{z^2}\right) D_n = 0. \quad (10)$$

It may be expressed in the form

$$D_n = \frac{J_{-n} - e^{in\pi} J_n}{\sin n\pi}, \quad (11)$$

which, however, requires a special evaluation when  $n$  is an integer. Using Schlöfli's formula

$$J_n(z) = \frac{1}{\pi} \int_0^\pi \cos(z \sin \theta - n\theta) d\theta - \frac{\sin n\pi}{\pi} \int_0^\infty e^{-n\theta - z \sinh \theta} d\theta, \quad (12)$$

$n$  being positive or negative, and  $z$  positive, we find

$$D_n(z) = \frac{1}{\pi} \int_0^\pi e^{n\theta - z \sinh \theta} d\theta + \frac{\cos n\pi}{\pi} \int_0^\infty e^{-n\theta - z \sinh \theta} d\theta - \frac{1}{\pi} \int_0^\pi \sin(z \sin \theta - n\theta) d\theta - \frac{i}{\pi} \int_0^\pi \cos(z \sin \theta - n\theta) d\theta, \quad (13)$$

the imaginary part being  $-J_n(z)$  simply. This holds good for any integral value of  $n$ . The present problem requires the examination of the form assumed by  $D_n$  when  $n$  is very great and the ratio  $z/n$  decidedly greater, or decidedly less, than unity.

In the former case we set  $n = z \sin \alpha$ , and the important part of  $D_n$  arises from the two integrals last written. It

104 Lord Rayleigh: *Further Applications of Bessel's*  
appears\* that

$$D_n = \left( \frac{2}{\pi z \cos \alpha} \right)^{\frac{1}{2}} e^{-i\rho}, \quad . \quad . \quad . \quad (14)$$

where  $\rho = \frac{1}{4}\pi + z\{\cos \alpha - (\frac{1}{2}\pi - \alpha) \sin \alpha\}$ ,  $. \quad . \quad (15)$

or when  $z$  is extremely large ( $\alpha=0$ )

$$D_n(z) = \left( \frac{2}{\pi z} \right)^{\frac{1}{2}} e^{-i(\frac{1}{4}\pi + z)}, \quad . \quad . \quad . \quad (16)$$

At a great distance the value of  $\phi$  in (9) thus reduces to

$$\phi = \left( \frac{2}{\pi kr} \right)^{\frac{1}{2}} \cos n\theta \cdot e^{i\{k(Vt-r) - \frac{1}{4}\pi\}}, \quad . \quad . \quad (17)$$

from which finally the imaginary part may be omitted.

When on the other hand  $z/n$  is decidedly less than unity, the most important part of (13) arises from the first and last integrals. We set  $n = z \cosh \beta$ , and then,  $n$  being very great,

$$D_n(z) = \left( \frac{\coth \beta}{2n\pi} \right)^{\frac{1}{2}} \{2e^{-t} - ie^t\}, \quad . \quad . \quad . \quad (18)$$

where  $t = n (\tanh \beta - \beta)$ .  $. \quad . \quad . \quad . \quad (19)$

Also, the most important part of the real and imaginary terms being retained,

$$D_n'(z) = - \left( \frac{\sinh \beta \cosh \beta}{2n\pi} \right)^{\frac{1}{2}} \{2e^{-t} + ie^t\}. \quad . \quad (20)$$

The application is now simple. From (9) with introduction of an arbitrary coefficient

$$\frac{d\phi}{dr} = kA e^{ikVt} \cos n\theta \cdot D_n'(kr). \quad . \quad . \quad . \quad (21)$$

If we suppose that the normal velocity of the vibrating cylindrical surface ( $r=a$ ) is represented by  $e^{ikVt} \cos n\theta$ , we have

$$kAD_n'(ka) = 1, \quad . \quad . \quad . \quad . \quad (22)$$

and thus at distance  $r$

$$\phi = e^{ikVt} \cos n\theta \frac{D_n(kr)}{kD_n'(ka)}, \quad . \quad . \quad . \quad (23)$$

or when  $r$  is very great

$$\phi = \cos n\theta \left( \frac{2}{\pi kr} \right)^{\frac{1}{2}} e^{i\{k(Vt-r) - \frac{1}{4}\pi\}} \frac{1}{kD_n'(ka)}. \quad . \quad . \quad . \quad (24)$$

\* Nicholson, B. A. Report Dublin, 1908, p. 595; Phil. Mag. vol. xix. p. 240 (1910); Macdonald, Phil. Trans. vol. ccx, p. 135 (1909).

We may now, following Stokes, compare the actual motion at a distance with that which would ensue were lateral motion prevented, as by the insertion of a large number of thin plane walls radiating outwards along the lines  $\theta = \text{constant}$ , the normal velocity at  $r=a$  being the same in both cases. In the altered problem we have merely in (23) to replace  $D_n, D_n'$  by  $D_0, D_0'$ . When  $z$  is great enough,  $D_n(z)$  has the value given in (16), independently of the particular value of  $n$ . Accordingly the ratio of velocity-potentials at a distance in the two cases is represented by the symbolic fraction

$$\frac{D_0'(ka)}{D_n'(ka)}, \quad \dots \quad (25)$$

in which

$$D_0'(ka) = -i \left( \frac{2}{\pi ka} \right)^{\frac{1}{2}} e^{-i(\frac{1}{4}\pi + ka)}. \quad \dots \quad (26)$$

We have now to introduce the value of  $D_n'(ka)$ . When  $n$  is very great, and  $ka/n$  decidedly less than unity,  $t$  is negative in (20), and  $e^t$  is negligible in comparison with  $e^{-t}$ . The modulus of (25) is therefore

$$\left( \frac{n/ka}{\sinh \beta \cosh \beta} \right)^{\frac{1}{2}} e^t, \quad \text{or} \quad \frac{e^{-n(\beta - \tanh \beta)}}{\sinh^{\frac{1}{2}} \beta}. \quad \dots \quad (27)$$

For example, if  $n=2ka$ , so that the linear period along the circumference of the vibrating cylinder ( $2\pi a/n$ ) is half the wave-length,

$\cosh \beta = 2, \quad \beta = 1.317, \quad \sinh \beta = 1.7321, \quad \tanh \beta = .8660,$   
and the numerical value of (27) is

$$e^{-.4510n} \div \sqrt{(1.732)},$$

When  $n$  is great, the vibration at a distance is extraordinarily small in comparison with what it would have been were lateral motion prevented. As another example, let  $n=1.1ka$ . Then (27)  $= e^{-.027n} \div \sqrt{(.4587)}$ . Here  $n$  would need to be about 17 times larger for the same sort of effect.

The extension of Stokes' analysis to large values of  $n$  only emphasizes his conclusion as to the insignificance of the effect propagated to a distance when the vibrating segments are decidedly smaller than the wave-length.

We now proceed to the case of the whispering gallery supposed to act by "total reflexion." From the results already given, we may infer that when the refractive index



is moderate, the escape of energy must be very small, and accordingly that the vibrations inside have long persistence. There is, however, something to be said upon the other side. On account of the concentration near the reflecting wall, the store of energy to be drawn upon is diminished. At all events the problem is worthy of a more detailed examination.

Outside the surface of transition ( $r=a$ ) we have the same expression (9) as before for the velocity-potential,  $k$  and  $V$  having values proper to the outer medium. Inside  $k$  and  $V$  are different, but the product  $kV$  is the same. We will denote the altered  $k$  by  $h$ . In accordance with our suppositions  $h > k$ , and  $h/k$  represents the refractive index ( $\mu$ ) of the inside medium relatively to that outside. On account of the damping  $k$  and  $h$  are complex, though their ratio is real; but the imaginary part is relatively small. Thus, omitting the factors  $e^{ikVt} \cos n\theta$ , we have ( $r > a$ )

$$\phi = A D_n(kr), \quad . \quad . \quad . \quad . \quad . \quad (28)$$

and inside ( $r < a$ )

$$\phi = B J_n(hr). \quad . \quad . \quad . \quad . \quad . \quad (29)$$

The boundary conditions to be satisfied when  $r=a$  are easily expressed. The equality of normal motions requires that

$$k A D_n'(ka) = h B J_n'(ha); \quad . \quad . \quad . \quad . \quad (30)$$

and the equality of pressures requires that

$$\sigma A D_n(ka) = \rho B J_n(ha), \quad . \quad . \quad . \quad . \quad (31)$$

$\sigma, \rho$  being the densities of the outer and inner media respectively. The equation for determining the values of  $ha, ka$  (in addition to  $h/k = \mu$ ) is accordingly

$$\frac{k D_n'(ka)}{\sigma D_n(ka)} = \frac{h J_n'(ha)}{\rho J_n(ha)}. \quad . \quad . \quad . \quad . \quad (32)$$

Equation (32) cannot be satisfied exactly by real values of  $h$  and  $k$ ; for, although  $J_n'/J_n$  is then real,  $D_n'/D_n$  includes an imaginary part. But since the imaginary part is relatively small, we may conclude that *approximately*  $h$  and  $k$  are real, and the first step is to determine these real values.

Since  $ka$  is supposed to be decidedly less than  $n$ ,  $D_n$  and  $D_n'$  are given by (18), (20); and, if we neglect the imaginary part,

$$\frac{D_n'(ka)}{D_n(ka)} = -\sinh \beta. \quad . \quad . \quad . \quad . \quad (33)$$

Thus (32) becomes

$$\frac{J_n'(ha)}{J_n(ha)} = -\frac{\rho k}{\sigma h} \sinh \beta, \quad . \quad . \quad . \quad (34)$$

the right-hand member being real and negative. Of this a solution can always be found in which  $ha = n$  very nearly. For \*  $J_n(z)$  increases with  $z$  from zero until  $z = n + .8065n^{\frac{1}{2}}$ , when  $J_n'(z) = 0$ , and then decreases until it vanishes when  $z = n + 1.8558n^{\frac{1}{2}}$ . Between these limits for  $z$ ,  $J_n'/J_n$  assumes all possible negative values. Substituting  $n$  for  $ha$  on the right in (34), we get

$$-\frac{\rho ka}{\sigma n} \sinh \beta, \quad \text{or} \quad -\frac{\rho}{\sigma} \tanh \beta, \quad . \quad . \quad . \quad (35)$$

while  $\cosh \beta = \mu$ . The approximate real value of  $ha$  is thus  $n$  simply, while that of  $ka$  is  $n/\mu$ .

These results, though stated for aerial vibrations, have as in all such (two-dimensional) cases a wider application, for example to electrical vibrations, whether the electric force be in or perpendicular to the plane of  $r, \theta$ . For ordinary gases, of which the compressibility is the same,

$$\rho/\sigma = h^2/k^2 = \mu^2.$$

Hitherto we have neglected the small imaginary part of  $D_n'/D_n$ . By (18), (20), when  $z$  is real,

$$\frac{D_n'(z)}{D_n(z)} = -\sinh \beta \frac{2e^{-t} + ie^t}{2e^{-t} - ie^t} = -\sinh \beta \cdot (1 + ie^{2t}) \quad (36)$$

approximately, with  $\cosh \beta = n/z$ . We have now to determine what small imaginary additions must be made to  $ha, ka$  in order to satisfy the complete equation.

Let us assume  $ha = x + iy$ , where  $x$  and  $y$  are real, and  $y$  is small. Then approximately

$$\frac{J_n'(x + iy)}{J_n(x + iy)} = \frac{J_n'(x) + iyJ_n''(x)}{J_n(x) + iyJ_n'(x)},$$

and

$$J_n''(x) = -\frac{1}{x} J_n'(x) - \left(1 - \frac{n^2}{x^2}\right) J_n(x).$$

Since the approximate value of  $x$  is  $n$ ,  $J_n''$  is small compared with  $J_n$  or  $J_n'$ , and we may take

$$\frac{J_n'(x + iy)}{J_n(x + iy)} = \frac{J_n'(x)}{J_n(x)} \left\{ 1 - iy \frac{J_n'(x)}{J_n(x)} \right\}. \quad . \quad . \quad (37)$$

\* See paper quoted on p. 100 and correction.

Similarly, if we write  $ka = x' + iy'$ , where  $x' = x/\mu$ ,  $y' = y/\mu$ ,

$$\frac{D_n'(x' + iy')}{D_n(x' + iy')} = \frac{D_n'(x') + iy' D_n''(x')}{D_n(x') + iy' D_n'(x')},$$

and in virtue of (10)

$$D_n''(x') = -\frac{\cosh \beta}{n} D_n'(x') + \sinh^2 \beta D_n(x'),$$

where  $\cosh \beta = n/x'$ . Thus

$$\frac{D_n'(x' + iy')}{D_n(x' + iy')} = \frac{D_n'(x')}{D_n(x')} \left\{ 1 + iy' \left( -\frac{\cosh \beta}{n} + \sinh^2 \beta \frac{D_n}{D_n'} - \frac{D_n'}{D_n} \right) \right\}.$$

Accordingly with use of (36)

$$\frac{D_n'(x' + iy')}{D_n(x' + iy')} = -\sinh \beta \left\{ 1 + ie^{2t} + iy' \left( -\frac{\cosh \beta}{n} + \sinh^2 \beta \frac{D_n}{D_n'} - \frac{D_n'}{D_n} \right) \right\} \quad (38)$$

Equation (32) asserts the equality of the expressions on the two sides of (38) with

$$\frac{h\sigma}{k\rho} \frac{J_n'(x)}{J_n(x)} \left\{ 1 - iy \frac{J_n'(x)}{J_n(x)} \right\} \quad (37)$$

If we neglect the imaginary terms in (38), (37), we fall back on (34). The imaginary terms themselves give a second equation. In forming this we notice that the terms in  $y'$  vanish in comparison with that in  $y$ . For in the coefficient of  $y'$  the first part, viz.  $-n^{-1} \cosh \beta$ , vanishes when  $n$  is made infinite, while the second and third parts compensate one another in virtue of (33). Accordingly (32) gives with regard to (34)

$$y = \frac{\sigma h}{\rho k} \frac{e^{2t}}{\sinh \beta} = \frac{\mu \sigma}{\rho} \frac{e^{-2n(\beta - \tanh \beta)}}{\sinh \beta}, \quad (39)$$

$$\text{in which} \quad \cosh \beta = \mu. \quad (40)$$

In (39)  $iy$  is the imaginary increment of  $ha$ , of which the principal real part is  $n$ . In the time factor  $e^{ikVt}$ , the exponent

$$ikVt = \frac{ihaVt}{\mu a} = \frac{inVt}{\mu a} \left\{ 1 + \frac{i(39)}{n} \right\}.$$





proved that the Hall coefficient in pure mercury and in bismuth amalgams is not greater than 0.00004 c.g.s. electromagnetic unit, the smallest value which he could detect. An experimental difficulty in the case of liquids, and the chief difficulty if the liquid is metallic, arises from the Lippman effect—the deformation of the liquid film produced by the electromagnetic forces unless the containing vessel is entirely filled. Amerio succeeded in overcoming this difficulty by giving a suitable shape to the containing vessel in one set of experiments, and by combining the observations made in his other experiments in a certain manner to be described below.

The importance of the subject in the theory of metallic conduction has made it seem advisable to attack the problem of the Hall effect in liquid mercury anew with apparatus permitting of greater precision than that attained by previous experimenters, and to investigate as well the Hall effect in solid mercury, on which no observations appear to have been published.

The general experimental arrangement was that ordinarily used in studying the Hall effect in metals by the method of direct deflexions. Several ways of holding the mercury were tried. In the final work it was confined between two thin glass plates which were separated by strips of ebonite, and cemented together, mercury tight, by water-glass. The dimensions of the last sheet of mercury upon which work was done in the liquid condition was  $5 \times 2 \times 0.090$  cm. The cavity could be exhausted, or pressure applied, by means of glass tubes connecting with the cavity. Platinum wires were used for both primary and Hall electrodes. The latter were connected directly to a Broca galvanometer, which with its leads had a resistance of about 3.2 ohms. Extraaneous electromotive forces were compensated by a potentiometer arrangement. The magnetic field was found to be uniform within about 1 per cent. over the region containing the mercury sheet. In the experiments on solid mercury freezing was effected by solid carbon dioxide and ether.

As is usual, readings were taken in sets of four, as follows:—

- |    |               |                         |                    |    |
|----|---------------|-------------------------|--------------------|----|
| 1. | Field direct, | primary current direct: | call the deflexion | A. |
| 2. | “             | “                       | “ reversed         | B. |
| 3. | “             | reversed                | “                  | C. |
| 4. | “             | “                       | direct             | D. |

Now, as Amerio states, at least three effects, superposed upon one another, can give rise to the deflexions: viz., one

( $\alpha$ ) which changes sign with the intensity of the magnetic field; a second ( $\beta$ ) which changes sign with the primary current; and a third ( $\gamma$ ) which reverses with both the field intensity and the current.  $\gamma$  has the characteristics of the Hall effect. If these are the only effects present

$$A + B + C + D = 0. \quad . \quad . \quad . \quad . \quad (1)$$

If only  $\alpha$  and  $\beta$  exist, that is, if the Hall effect is zero,

$$A + C = B + D = 0. \quad . \quad . \quad . \quad . \quad (2)$$

*Liquid Mercury.*—Three different cavities for holding the mercury were used; several sets of readings were taken with each. The strength of the magnetic field ranged from about 10,000 gauss to 22,400 gauss; the primary current from 0.14 ampere to 3.07 amperes. Although the work on the first two cavities indicated the absence of the Hall effect, the unsteadiness of the galvanometer was such that one could not say with certainty that the observations indicated a coefficient smaller than 0.00010 electromagnetic unit. With the third cavity, however, the steadiness and the sensitiveness were improved. A pressure of about three hundred grams per sq. cm. was applied to the mercury in the cavity. (Greater pressure produced no improvement.) Readings were taken with this cavity which satisfied exactly equations (1) and (2). Due allowance being made for unsteadiness, which prevented readings being taken to less than  $\frac{1}{2}$  mm., we find that this experiment indicates the absence of a Hall effect in liquid mercury with a coefficient larger than 0.00002 electromagnetic unit, one-half the smallest value Amerio could observe.

*Solid Mercury.*—In this part of the work the galvanometer was much more nearly steady than before. The thermal electromotive force in the circuit was large, but was very nearly constant. No vibration of the image could be detected, but in some cases there was a slight drift which was easily compensated. By taking these precautions readings were easily taken to one-fifth mm.

Two different strengths of field, 12,100 and 10,000 gauss respectively, and two different strengths of primary current, 2.00 and 3.93 amperes respectively, were used. In each case  $A = B = C = D = 0$ , showing that  $\alpha = \beta = \gamma = 0$ .

The thickness of the sheet of mercury was 0.080 cm. The electromotive force which would produce one mm. deflexion on the galvanometer scale was  $3.23 \times 10^{-8}$  volt. The Hall coefficient  $R$  which, if present, would produce

112 Dr. Russell and Mr. Chadwick on the  $\gamma$  Rays of  
one mm. deflexion is

$$R = \left( \frac{3 \cdot 23 \times 0 \cdot 080}{12,100 \times 0 \cdot 393} = 0 \cdot 000054 \right) \text{ electromagnetic unit.}$$

Hence this experiment indicates that in solid mercury there is no Hall coefficient larger than 0·000011 electromagnetic unit, which is about one-fourth that of tin.

After this investigation was begun, Alterthum \* published some theoretical work indicating the absence of a Hall effect in liquids; but the experiments described here show that the observations which have been made on liquid mercury cannot be adduced to support that theory.

I am indebted to Professor Barnett for proposing this investigation and for many valuable suggestions. For similar suggestions I am also indebted to Professor A. W. Smith.

The Physical Laboratory,  
Ohio State University,  
June 1, 1913.

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XI. *The  $\gamma$  Rays of Polonium, Radium, and Radioactinium.*  
By A. S. RUSSELL, M.A., D.Sc., Carnegie Research Fellow  
of the University of Glasgow, and J. CHADWICK, M.Sc.,  
Beyer Fellow of the University of Manchester†.

THE work, an account of which is given in this paper, is a continuation of that already described in two previous communications‡. In the first of these it was shown that when the  $\alpha$ -rays of radium C impinge upon plates of different materials, a small but definite amount of  $\gamma$ -radiation is produced. The amount of this radiation was, however, too small to permit of analysis. Later we showed that strong preparations of ionium and of radiothorium, when freed from all bodies emitting  $\beta$ - and  $\gamma$ -rays, emitted a small quantity of  $\gamma$ -radiation. For various reasons the radiation emitted by radiothorium was not analysed. Analysis of the radiation of ionium, however, showed that it consisted of three types of rays varying widely in penetrating power and in intensity. A small quantity of  $\beta$ -radiation, too large to be ascribed to thorium products, but too small to be analysed, was found also to accompany the  $\gamma$ -radiation from ionium.

\* *Ann. der Phys.* no. 15, 1912, p. 933.

† Communicated by Prof. E. Rutherford, F.R.S.

‡ J. Chadwick, *Phil. Mag.* vol. xxv. p. 193 (1913); J. Chadwick & A. S. Russell, *Proc. Roy. Soc. A.* vol. lxxxvii. p. 489.

The results obtained with ionium raised the question whether this  $\gamma$ -radiation is emitted by the disintegrating atoms themselves, *i. e.* by the ionium, or by the thorium with which it was mixed and from which it could not be separated. Had the separation of thorium from ionium been possible, this question would not have been a difficult one to answer, but, as is well known, this cannot be done. To attack this problem therefore, and to extend our knowledge of the nature of the  $\gamma$ -rays excited by the  $\alpha$ -rays, we have continued our work by investigating the  $\gamma$ -rays emitted by polonium, by the element radium itself, and by radioactinium.

The five bodies we have investigated, *viz.* ionium, radiothorium, polonium, radium, and radioactinium, expel, in addition to their  $\alpha$ -rays, a small quantity of  $\gamma$ -radiation. It seems probable therefore that all  $\alpha$ -ray bodies, when completely freed from all products and impurities emitting  $\beta$ - and  $\gamma$ -rays, emit a measurable quantity of  $\gamma$ -radiation, provided the quantity of material under investigation is sufficiently great. In the  $\gamma$ -ray electroscope used by us, which is a large one of the ordinary type with a very thin window through which the rays pass, a quantity of about 1 milligramme of radium, or a quantity of another body, expelling per second the same number of  $\alpha$ -particles, is necessary to obtain measurable effects.

We found that the  $\beta$ -radiation from ionium under our experimental conditions was only about 10 per cent. in intensity of the  $\gamma$ -radiation, and a result of a similar nature has been found with polonium. These  $\alpha$ -ray bodies emit, therefore, a very small amount of  $\beta$ -radiation. There are other  $\alpha$ -ray bodies, however, such as radium, thorium X, and radioactinium, which emit considerable quantities of  $\beta$ -radiation. An investigation of the  $\gamma$ -rays of one of these, for instance radium, is therefore likely to show that it emits  $\gamma$ -rays corresponding to its  $\beta$ -rays, as well as  $\gamma$ -rays produced by the  $\alpha$ -rays.

The great difficulty in this research has been to obtain a sufficiently large quantity of polonium. By the kindness of Professor Rutherford the strongest source of polonium available in the laboratory was obtained, but the intensity of the  $\gamma$ -rays was disappointingly small. For this reason we were unable to obtain, either in accuracy or in detail, the results we hoped for when the work was commenced, and for which the methods described in this paper were worked out.



*Preparation of pure Polonium and of Radium D and E.*

The method of separation of polonium which we employed consisted of a combination of ordinary chemical methods, electrolysis, and volatilization. As it was possible by these methods to prepare at the same time radium D and radium E in the pure state, and as it was necessary to do this for another research, a detailed account will now be given of the separation of all of these bodies, though there is nothing essentially new either in principle or in details in the methods employed.

Preliminary experiments were carried out on an old preparation of radium (D+E+F) containing, as impurity, lead sulphide. The object of these experiments was to obtain each of these substances in the form of a thin film on a metal as nearly as possible in quantitative amount, and free from active and inactive impurities. When these experiments were completed operations were carried out on larger quantities.

The largest source of polonium in the laboratory was the accumulation of radium (D+E+F) in a preparation of 31 milligrammes of radium bromide which had been sealed up and untouched for six or seven years. This material was dissolved in hot water containing just enough HCl to effect solution. To this was added a solution containing 1 milligramme lead chloride and the whole evaporated to about 10 c.cm. A plate of copper well polished on both sides was rotated in this solution for about two hours. Preliminary experiments had shown that under these circumstances about 95 per cent. of the polonium is deposited on the copper. A fair proportion of radium E is also deposited with it, but no radium D if lead be present. The copper plate was then removed, carefully washed, and set aside.

The radium solution was diluted, and heated, and a solution of  $\text{H}_2\text{S}$  added to it in excess. This precipitated as sulphides all the copper which had been previously dissolved off the electrode and also the lead which had been previously added. The precipitate contained the whole of the radium D, and all the radium E and polonium not deposited on the copper. It was dissolved in  $\text{HNO}_3$ , the solution evaporated to dryness, and the material redissolved in hot water containing a little HCl. To obtain the radium D from this solution it was treated as follows. Three milligrammes of aluminium in the form of chloride were added to the solution, and then ammonia in excess. This precipitates everything except the copper. It is necessary to remove the copper at this stage since the subsequent operation of separating radium D from

radium E by depositing the latter on a plate of nickel does not lead to satisfactory results when copper is present. The aluminium is added to act as a nucleus for the small quantity of lead hydroxide precipitated by the ammonia. The precipitate of lead and aluminium was then dissolved in the minimum quantity of HCl and evaporated to a volume of a few cubic centimetres. A plate of polished nickel was rotated in this solution for half an hour and then removed. This removes from the radium D practically all the radium E and polonium.

A small quantity of nickel goes into solution. The solution is then treated with excess of ammonia. The nickel in the solution is not precipitated by the ammonia, but the lead and the aluminium containing the radium D are precipitated quantitatively. This precipitate was then filtered off and used as source on the filter-paper. It is not advisable, nor is it for any purpose necessary, to separate the lead and the radium D from the aluminium. Two preparations of radium D prepared in this way from two different quantities of old radium were used by Rutherford and Richardson in their work on the  $\gamma$ -rays of this substance\*.

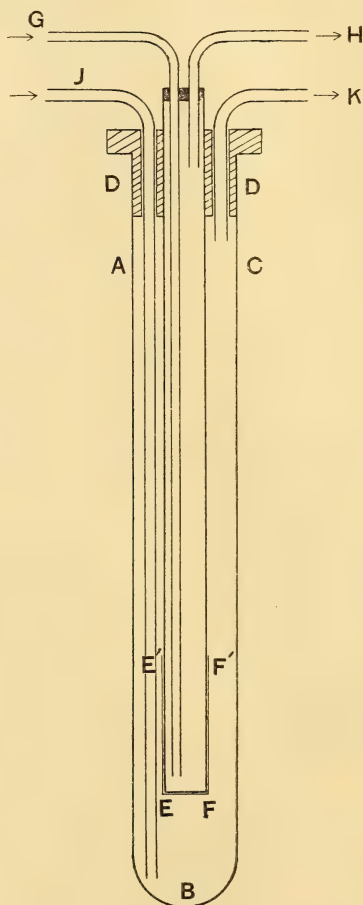
The radium E grown from these radium D preparations is separated as follows. The preparation is dissolved in the minimum quantity of HCl, evaporated till the solution contains a few c.cm. only, and a clean nickel plate varnished on one side is rotated in it for half an hour. This removes nearly all the radium E but no radium D whatever. The radium E deposited on nickel acts as a convenient source of that body. If it is necessary to have it deposited on another metal, it is first deposited on nickel and then transferred to the other metal by volatilization. The details of this operation are given below. To the solution from which the radium E has been removed ammonia in excess is added. The precipitated lead and aluminium containing the radium D are filtered off from the nickel and used as a source on the filter-paper.

The large quantity of polonium on the copper plate was freed from the radium E deposited with it by volatilization in air. Preliminary experiments on the volatilization of these bodies showed that in air at a temperature of  $900^{\circ}$  C. polonium is completely volatilized in a short time, while at this temperature little or no radium E is volatilized. This fact was made use of in separating the polonium from the radium E. To volatilize radium E in air it was found

\* E. Rutherford & H. Richardson, *Phil. Mag.* vol. xxvi. p. 324 (1913).

necessary to employ a temperature greater than  $1100^{\circ}$ , but in hydrogen it can be volatilized in a short time at  $900^{\circ}$ . The second of these facts was used in transferring radium E from metal to metal in connexion with the work of Rutherford and Richardson\*.

The apparatus used in volatilizing these substances is shown in the figure.



ABC is a thick porcelain tube, 25 cm. in length and 2.4 cm. inside diameter, closed at one end B. The other end is closed by an ebonite cork D through which a brass cylinder passes centrally. The diameter of this cylinder is

\* Phil. Mag. vol. xxvi. p. 324 (1913).

11 mm., and its end EF is about 3 to 4 cm. from the end of the porcelain tube. This inner cylinder can be kept cool, when the outer is heated, by circulating cold water through it, the water running in at G and out at E. A long tube of quartz J passes through D and reaches almost to the bottom of the porcelain tube. This enables the apparatus to be filled with hydrogen if required. The hydrogen passes out of the tube through K. The active material deposited on a metal was placed at B. The metal on to which it was to be volatilized was wrapped round the cooled tube as high as E'F'. A cap of the same material covered the end of the tube EF.

The tube ABC was placed in a furnace so that the temperature of three or four centimetres of it at the end B was about  $900^{\circ}$ , the tube being water-cooled. The active plate containing the polonium and the radium E was placed at B. Aluminium was wrapped round the cooled tube. After two hours the volatilization was stopped. It was then found that the copper plate, now covered with a thin film of oxide, was quite free from polonium and contained radium E only. The aluminium, on the other hand, contained no radium E, for it emitted very little  $\beta$ -radiation and this did not decay with time. The greater part of the polonium was deposited on the cap which had been wrapped round EF. Some was deposited on the portion E'EFF' in the vicinity of the end of the tube.

Many transference experiments were carried out in this way with polonium. When small quantities were dealt with, if the experiment were carefully carried out, there was usually not much loss of material in volatilizing from one metal to another, about 95 per cent. of material being obtained on the second metal. It was more difficult to say what proportion was obtained when large quantities were used.

In transferring radium E from one metal to another the experiment was carried out similarly. Radium E was placed at B, the same temperature was employed, but the volatilization was conducted in a gentle stream of hydrogen gas. The transference was never quantitative, but the loss of material was rarely more than 10 per cent. of the whole.

#### *The $\gamma$ -radiation of Polonium.*

The preparation of polonium deposited on aluminium foil was mounted on a cardboard frame and suspended between the pole-pieces of a powerful electromagnet. The faces of the pole-pieces were 10 cm.  $\times$  16.5 cm. and were 7 cm. apart.



They were covered with thick cardboard to minimise diffuse reflexion of  $\beta$ - and  $\gamma$ -rays from them. The electroscope was of the ordinary type, 15 cm.  $\times$  10 cm.  $\times$  10 cm., and was placed at the end of the pole-pieces. In the side against the pole-pieces was cut an opening 8 cm. by 8 cm., which was covered with aluminium foil .0013 cm. thick. The distance of the polonium preparation from this side of the electroscope was 5 cm. The strength of the magnetic field usually employed to deviate the  $\beta$ -rays completely was about 1500 gauss. Under these conditions the polonium preparation gave a leak of 6 scale-divisions per minute when the magnetic field was applied. As no  $\alpha$ -rays could possibly enter the electroscope, and as the preparation was free from other products, this leak must be due to the  $\gamma$ -rays of polonium itself. The absorption of the radiation by thin sheets of aluminium was determined, and the curve obtained showed the presence of one type of radiation only. The mean value of  $\frac{\mu}{D}$  (cm.)<sup>-1</sup>—the absorption coefficient divided by the density

—obtained from several determinations was 230. This value corrected for obliquity of the beam becomes 215. Although the polonium was deposited on several different metals, this type of radiation was always obtained. It cannot, therefore, be due to the impact of the  $\alpha$ -particles against the aluminium, and must be due to the polonium atoms themselves.

If a harder type of radiation is emitted by the polonium, one would expect it to be of about the same penetrating power as the soft  $\gamma$ -rays of radium D. In order that this point might be more thoroughly investigated, Professor Rutherford kindly allowed us to use the electroscope filled with methyl iodide described by Rutherford and Richardson\*. Some slight evidence of the existence of a harder type was obtained, but its intensity was only about 2 per cent. of the natural leak. This evidence cannot, therefore, be regarded as definite, and if a harder type does exist it must be very small in intensity compared with the type described above, and would require powerful preparations to permit of its analysis.

When the magnetic field was not applied the leak in the electroscope was increased about 1 division a minute. This difference is due to  $\beta$ -rays emitted probably by polonium, for different preparations of polonium gave a  $\beta$ -radiation proportional in amount to the  $\gamma$ -radiation. It is possible, but unlikely, that the same proportion of radium D and E would be present in preparations of polonium which had been

\* Phil. Mag. vol. xxvi. p. 324 (1913).

subjected to different processes of purification. This  $\beta$ -radiation was soft, but its amount was too small to be investigated further. It was, however, much more penetrating than the  $\beta$ -rays described by Bumstead and McGougan\*, which were shown to be completely absorbed by  $0.64 \times 10^{-4}$  cm. aluminium.

*Quantitative determination of the Intensities of strong sources of Polonium.*

The polonium was next transferred from aluminium to different metals to see whether or not the  $\alpha$ -rays of polonium set up  $\gamma$ -radiation in these metals. It was necessary, therefore, to have a means of measuring accurately by  $\alpha$ -rays the strength of the sources employed. The quantities of polonium to be measured varied widely in intensity, from about that in equilibrium with .01 mg. radium to that in equilibrium with 2 mg. The usual methods of measuring bodies which expel  $\alpha$ -rays, *e. g.* the scintillation method of counting particles, are much too sensitive for quantities of this magnitude. The ionization current produced by such large amounts is, however, sufficiently great to be measured by a galvanometer, and this was the method employed. To enable quantities of widely different magnitudes to be measured without change in the apparatus, a balance method was used which consisted simply in sending a current through a galvanometer in the opposite direction to the ionization current. The current was provided by a storage-cell and could be varied by means of a resistance-box. We found in this way that the actual amount of polonium separated by us from 18 mgrms. of radium metal after six years' growth was that in equilibrium with 1.3 mgrms. of radium. The theoretical amount, provided the polonium had been separated quantitatively, is 3.6 mgrms., taking the period of radium D as 16.5 years. There is a serious discrepancy between these numbers. We found a discrepancy of a similar order between the theoretical and experimental amounts of polonium separated from 5 mgrms. of old radium which had been left untouched for seven years. We cannot offer any adequate explanation of these results. It is most unlikely that we obtained a third only of the total quantity of polonium, since the separations were repeated without obtaining a further quantity of polonium. On the other hand, Antonoff's method of determining the period of radium D was equivalent to the above, and his value used in our calculation is very similar to that obtained previously by Meyer and von Schweidler.

\* Bumstead & McGougan, *Phil. Mag.* vol. xxiv. p. 462.

*Excitation of  $\gamma$ -rays by the  $\alpha$ -rays in Copper and in other metals.*

The main quantity of polonium was transferred from aluminium to copper by dissolving the aluminium in HCl, evaporating the solution to dryness, dissolving the aluminium chloride in water, and rotating a clean copper plate varnished on one side in the solution for an hour. The  $\gamma$ -radiation from this plate was then analysed in the usual way.

Both in penetrating power and in intensity, the radiation from polonium on copper was different from what it had been when the polonium was deposited on aluminium. The intensity measured under the same experimental conditions was, for equal quantities of polonium, about three times greater on copper than on aluminium. This amount varied, however, according as the copper oxide and chloride on the surface of the copper was quite dry or not. Two types of radiation were found to be present. One was the same in intensity and penetrating power as that emitted from aluminium, with a value of  $\frac{\mu}{D} = 215$ , the other giving a value  $\frac{\mu}{D} = 1300$  about. This new radiation must be due to excitation in the copper by the  $\alpha$ -rays. It is possibly the characteristic radiation of copper in series L.

The active material was next transferred back to aluminium by volatilization, and the intensity measured again. No other radiation except that having a value of  $\frac{\mu}{D} = 215$  could be detected, and the copper was inactive. Part of the main quantity of polonium was then deposited on platinum foil and the radiation investigated. No evidence of an excited radiation was obtained. The rest of the polonium was volatilized on to lead foil. The amount and absorbability of the radiation in this case were approximately the same as when the polonium was deposited on aluminium, except that the absorption produced by the first thickness of aluminium was rather greater than before. The difference, however, was 0.2 div. per minute only, and therefore too small to be regarded as definite.

It is thus seen that when polonium is deposited on metals of high atomic weight like platinum and lead, the excited radiation, if produced at all, is small compared with that excited in an element of low atomic weight similar to copper.

Experiments with other metals were not carried out owing to the difficulty of measuring the small effects to be obtained with the quantity of polonium at our disposal. Such experiments can be most conveniently carried out with an  $\alpha$ -ray body which can be obtained in considerable quantity, such as radium C. The experiments with polonium show that an excited radiation can be produced by  $\alpha$ -rays in at least one metal, a phenomenon that has already been found with radium C. In this connexion it may be mentioned that recently Rutherford and Richardson\*, using a source of radium C on a nickel plate, found that the  $\alpha$ -rays produced in nickel a soft  $\gamma$ -radiation probably belonging to series K.

### *The $\gamma$ -rays of Radium.*

Hahn and Meitner† found that radium, completely freed from all its short- and long-lived products, emitted a radiation of a very soft type having a coefficient of absorption  $\mu$  in aluminium of about  $312 \text{ (cm.)}^{-1}$ . This result was confirmed by Kolowrat‡, who found a value of  $\mu$  of  $200 \text{ (cm.)}^{-1}$ . This radiation is a  $\beta$ - and not a  $\gamma$ -radiation, for it is capable of being deflected by a magnetic field, and has been shown to consist of two groups of homogeneous rays expelled with velocities 0.52 and 0.65 of the velocity of light. The amount of this radiation measured in the ordinary way was about 2 per cent. of the total  $\beta$ -radiation of radium in equilibrium with its products. So far, however, no one has carried out an investigation to determine if a  $\gamma$ -radiation accompanies this  $\beta$ -radiation.

Several investigators, however, have pointed out that if a radium solution, from which the radium D, E, and F have been removed, be evaporated slowly to dryness in such a way that all the emanation is expelled and all the short-lived products have time to decay, the intensity of the  $\gamma$ -radiation is about 2 per cent. of the initial activity, if the rays are measured through a sufficient thickness of material to absorb the  $\beta$ -rays completely. It was natural in the early experiments to attribute this radiation to the presence of some radium C which had not been removed by the methods employed. In the light of subsequent work, it is possible that this radiation, or at least a part of it, is emitted by the radium atoms themselves, and is not to be ascribed to radium B and C.

\* Rutherford & Richardson, *Phil. Mag.* vol. xxv. p. 722.

† Hahn & Meitner, *Phys. Zeit.* vol. x. p. 741 (1909).

‡ Kolowrat, *Le Radium*, vol. vii. p. 269 (1910).



An investigation of the  $\gamma$ -radiation of a quantity of radium at its minimum  $\alpha$ -ray activity has therefore been carried out by us.

A radium solution, from which the radium D, E, and F had been completely removed some days previously, containing about five milligrammes of radium bromide, was heated on a water-bath for six hours, the amount of solution being kept constant by adding water. We experienced some difficulty in keeping the radium in solution, and had to add some HCl to prevent the radium from being precipitated. Every twenty minutes a little air was bubbled through the solution to remove any emanation not otherwise expelled. After about six hours' boiling the solution was evaporated to dryness as rapidly as possible, first on a water-bath and later at a temperature of about  $200^{\circ}$ . The evaporating dish containing the radium was then placed at a distance of 10 cm. from the side of the electroscope between the pole-pieces of the magnet. Measurements of the  $\beta$ - and the  $\gamma$ -ray activity were made through various thicknesses of aluminium until the growth of radium B and C interfered with the measurements. Several successful experiments were made, and it was found that the activity of the radium was reduced to about the same amount each time. The  $\beta$ -ray activity of the radium immediately after evaporation was nearly 250 div. per min., and the  $\gamma$ -ray activity 4 div. per min. Although measurements of the rise of the activity of the preparation showed that little or no radium B or radium C was present initially, yet absorption measurements of the  $\beta$ -radiation indicated the presence of a hard radiation in addition to the soft. The amount of this hard radiation was about 10 div. per min., and it had an absorption coefficient of about  $20 \text{ (cm.)}^{-1}$  in aluminium. We had hoped that absorption measurements of the  $\beta$ -radiation would afford a test of the purity of the radium, but the presence of these penetrating  $\beta$ -rays prevented this.

Some results will now be given which show that the  $\gamma$ -radiation measured by us was due to radium, and not to its products. In one experiment the  $\beta$ -rays through a thickness of 0.057 cm. aluminium varied from 9.4 to 21.5 during the course of an experiment, the  $\gamma$ -rays in the same time and through the same thickness varied only from 2.8 to 3.5. In another experiment the  $\beta$ -rays increased from 10 to 17 through the same thickness of aluminium as above, while the  $\gamma$ -rays increased only from 3.4 to 3.6. Even if the hard  $\beta$ -rays had been due to radium C the  $\gamma$ -rays could not be due to it, and had radium C been present there would have been an initial decay.

The absorption of the  $\gamma$ -radiation of radium at the time of its minimum activity was compared with that of radium in equilibrium with its products, radium A, B, and C. In the first column of Table I. below is given the thickness of aluminium, in the second are the intensities of the radiation from radium in equilibrium with radium A, B, and C, through these thicknesses, where the initial intensity has been put at 100, in the third the relative intensities of the  $\gamma$ -radiation from radium at its minimum activity. The table shows that the  $\gamma$ -rays of radium itself are much less penetrating than those of its products radium A, B and C.

TABLE I.

Thickness of Aluminium (cm.).	Intensity of $\gamma$ -rays from Ra+Ra(A+B+C) in equilibrium.	Intensity of $\gamma$ -rays from radium itself.
0.08	100	100
0.57	97.6	87
1.33	94.5	78
2.66	—	72
3.23	91.3	—
1.0	81.6	62
1.3	—	56
2.0	73.9	45
2.3	—	33

The intensity of the  $\gamma$ -radiation of radium was about 1 to  $1\frac{1}{2}$  per cent. of that of radium and its products in equilibrium measured through 0.1 cm. of aluminium. This percentage would be less if the measurements were conducted through a greater thickness of aluminium or of lead.

Absorption measurements of the radium  $\gamma$ -rays by small thicknesses of aluminium showed the presence of a very soft type of radiation which had a value of  $\mu_D$  between 100 and 150. The amount of this type varied between 1.5 and 2.5 div. per min. according to the distribution of the active material. Owing to the growth of emanation and of radium B and C, the  $\gamma$ -ray activity began to rise steadily after an hour. Emanation also diffused into the electroscope and increased the natural leak. Consequently it was difficult to make accurate measurements, and though it can be said definitely that radium emits three types of  $\gamma$ -radiation, the absorption coefficients given are only approximate. The softest type gave about 2 div. per min., and had a value of

$\frac{\mu}{D}$  between 100 and 150. The amount of the intermediate type was about 1 div. per min. and  $\frac{\mu}{D}$  about 6. The hardest type gave about 3 div. per min. and gave  $\frac{\mu}{D}$  about  $\cdot 09$  or  $\cdot 10$ .

By comparison with the radiations from other bodies, and from the proportion of the different types, it would appear that the two harder types are connected with the  $\beta$ -radiation while the softest type is due to  $\alpha$ -rays. It is of course possible that the intermediate type is also due to  $\alpha$ -rays.

### *Radioactinium.*

An examination has also been made of the radiations of radioactinium. Hahn and Meitner\* showed that, besides  $\alpha$ -rays, the body emitted soft  $\beta$ -rays, and a radiation which was either a hard  $\beta$ -radiation or a soft  $\gamma$ -radiation. An actinium preparation was taken and its  $\gamma$ -radiation was found to be about 23 div. per min. The radioactinium was separated from this by chemical operations and its radiations examined. We found that besides the soft  $\beta$ -rays described by Hahn and Meitner, there was a  $\gamma$ -radiation of about 5.5 div. per min. This  $\gamma$ -radiation was found to consist of two types, the absorption coefficients of which were only approximately determined. The measurements showed that these types were very slightly harder than the two hard types emitted by ionium, the values of  $\frac{\mu}{D}$  (cm.)<sup>-1</sup> being about 8 and 0.1.

During this investigation we thought we had succeeded in showing that radioactinium is complex, and in a letter to 'Nature' of 26th December, 1912, we stated that radioactinium consists of two products, the second of which has a half value period of about 12 hours. Subsequent work showed that the actinium preparation we had been using contained a small amount of either mesothorium or radiothorium. This fact, and also the nature of the chemical properties, suggested that the new product was really thorium B, although the tests for thorium emanation indicated that the amount of the contamination with thorium products was not sufficient to vitiate the results. However, as both of us are leaving Manchester, and as neither of us will have an opportunity of continuing the work for some time, we think it is better to withdraw our statement of the complex nature of radioactinium.

\* Hahn & Meitner, *Phys. Zeit.* vol. ix. p. 697 (1908).

*Summary.*

(1) Methods of separating radium D, radium E, and polonium in the pure state in a form suitable for physical work are described in detail.

(2) The  $\gamma$ -radiations from polonium, from radium, and from radioactinium have been investigated. Polonium emits  $\gamma$ -radiation of one type only, having a value of  $\frac{\mu}{D} = 215 (\text{cm.})^{-1}$ .

This radiation is due to the polonium itself, and is not due to impact of the  $\alpha$ -rays of polonium against the metal on which it is deposited.

The  $\alpha$ -rays of polonium are able to excite a soft  $\gamma$ -radiation in copper, though not to an appreciable extent in platinum or in lead. This excited radiation in copper is possibly the characteristic radiation of copper in Series L.

A very small quantity of  $\beta$ -radiation is also emitted by polonium.

(3) Radium itself freed from its products has been found to emit  $\gamma$ -rays. This  $\gamma$ -radiation appears to consist of three types, one of which is much softer than the other two. The softest type has a value of  $\frac{\mu}{D} (\text{cm.})^{-1}$  in aluminium of about

130, and the other two types of 6 and 0.1. The intensity of the  $\gamma$ -radiation from radium itself is about 1 to  $1\frac{1}{2}$  per cent. of that of radium in equilibrium with its short-lived products.

(4) The quantity of polonium separated from two different quantities of old radium of known age was about two to three times smaller than is to be expected if the separation were approximately quantitative and the period of radium D were 16.5 years.

(5) Radioactinium emits two types of  $\gamma$ -rays, the value of  $\frac{\mu}{D} (\text{cm.})^{-1}$  in aluminium of one being about 8, and that of the other about 0.1. The results given in a previous preliminary communication regarding the existence of a new product in the actinium series are withdrawn.

We have to express our warmest thanks to Professor Rutherford for placing at our disposal the apparatus and valuable radioactive material necessary for the carrying out of the work, and for his stimulating interest and advice at all times.



XII. *Crossed Spectra obtained by Combinations of Different Interferometers, and their Applications to the Measurement of Difference in Wave-lengths.* By H. NAGAOKA, Professor of Physics, and T. TAKAMINE, Graduate in Physics, Imperial University, Tokyo\*.

[Plate I.]

THE method of crossed spectra introduced by Kundt was utilized by Gehrecke and v. Baeyer † for discriminating the ghosts by means of interference points produced by Lummer-Gehrecke plates placed at right angles to each other. This effective method can be applied to combinations of different interferometers, and the crossed spectra thus obtained may sometimes be utilized for the purpose of accurately determining the difference in wave-lengths. We have studied some of these combinations in experiments relating to the structure of mercury lines and their Zeeman effect, and we believe that crossed spectra will be of some interest to those engaged with spectroscopic work.

The spectra produced by the combination of Lummer-Gehrecke plates were treated by Gehrecke, v. Baeyer, and Janicki ‡, so that it will be unnecessary to discuss them here. We tried crossing a plane grating with an echelon, an echelon with another echelon, an echelon with a Lummer-Gehrecke plate, a Lummer-Gehrecke plate with a Fabry-Perot air-plate, and a Fabry-Perot air-plate with an echelon. The first way of crossing was not effective on account of low resolving power of the grating, the second, though somewhat better, was not at all comparable with the advantages that can be gained by the last three methods of combination; on this account we limit our discussion to these three kinds of crossed spectra.

*Echelon Grating and Lummer-Gehrecke Plate combined.*—The echelon grating and the plane-parallel plate used in the present experiment were made by Hilger, and had the following dimensions and constants:—

Echelon: number of plates 35, thickness of plate 9.350 mm., step 1 mm., length 32.73 cm.,

$$\begin{aligned}\delta\lambda \text{ max.} &= 580.5 \text{ m.}\text{\AA}.\text{U. for } 5790 \\ &= 576.0 \quad \quad \quad \text{,,} \quad \quad \text{,, } 5769. \\ &= 509.0 \quad \quad \quad \text{,,} \quad \quad \text{,, } 5461.\end{aligned}$$

\* Communicated by the Authors.

† Gehrecke and v. Baeyer, *Ann. der Phys.* xx. p. 269 (1906).

‡ Janicki, *Ann. der Phys.* xxxix. p. 439 (1912).

Plate: length 20 cm., breadth 3.5 cm., thickness 1.0912 cm.

$$\begin{aligned}\delta\lambda \text{ max.} &= 120.9 \text{ m.}\text{\AA}.\text{U. for } 5790 \\ &= 120.0 \quad \quad \quad \text{,,} \quad \text{,,} \quad 5769 \\ &= 106.6 \quad \quad \quad \text{,,} \quad \text{,,} \quad 5461.\end{aligned}$$

We have published in another place\* our results concerning the structure of mercury lines obtained by crossing the echelon-grating spectrum with that given by the plate, so that it will be unnecessary to reproduce them here. When only one instrument is used, there is much difficulty in interpreting the results owing to overlapping of several orders of spectra, and to the appearance of ghosts. These two points are the chief objections raised by Wood† against the use of echelon or plate, but the difficulties can be overcome by simply crossing the instruments.

As regards the elimination of ghosts, the discussion given by Gehrecke and v. Baeyer for a combination of plates applies equally to that of echelon and plate. The ambiguity as to the orders of spectra is easy to settle, as the interference points belonging to the same order of spectrum lie on a parabola, whose position and dimension are easily determined. The simple process of arranging the points on a section paper is sufficient to decide this puzzling question, which can hardly be answered when an interferometer is used singly.

It will not be out of place to compare Wood's measurements of the satellites of mercury lines observed with a concave grating with our results made on crossed spectra.

	Wood.	Nagaoka and Takamine.
5790	+ 222 m.Å.U.	+ 224
	+ 164	+ 164
	+ 131	+ 130
	0	0
	— 124	— 119
	— 191	— 191
	— 944	— 938
	— 1007	— 999
5769	+ 42	+ 44
	0	0
	— 55	— 50
	— 112	— 121

\* Nagaoka and Takamine, Proc. Phys. Soc. xxv. p. 1 (1912).

† Wood, Phil. Mag. xxv. p. 443 (1913).

(Centre displaced +14).

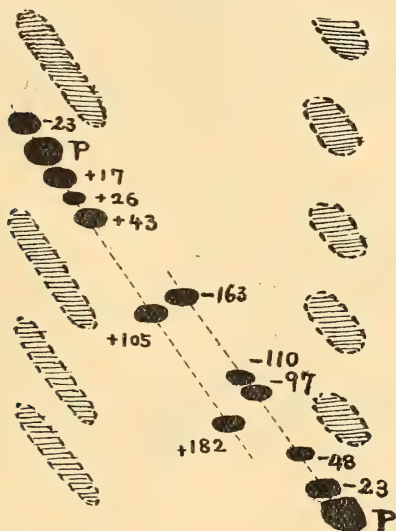
4359	{	+ 212	+ 226*	—
		+ 168	+ 182	+ 182
		+ 130	+ 144*	—
		+ 91	+ 105	+ 105
		+ 29	+ 43	+ 43
		—	—	+ 26**
		—	—	+ 17**
		0	0	0
		— 34	— 20	— 23
				— 48**
		— 111	— 97	— 97
		— 124	— 110	— 110
		— 174	— 160	— 163
		— 219	— 205*	—
		— 282	— 268*	—

Wood's values agree tolerably well with ours for satellites of two lines 5790 and 5769 ; the presence of the lines —938 and —999 in the former has been confirmed in our case by arranging the interference points on parabolas before mentioned ; further, the existence of the second satellite on the negative side of the latter can hardly be doubted. As to the satellites of the violet line 4359, we have to remark that the position of the principal line is rather doubtful. There is a satellite very close to the principal and another not far from it on the positive side. In order to bring Wood's measurement in harmony with ours, it is necessary to displace the centre towards the negative side by about 14 m.A.U. ; by so doing the numbers in the second column were obtained, agreeing quite well with ours. We missed the lines marked with an asterisk, and Wood those with double asterisks. This must be ascribed to the high resolving power of echelon and plate, while the new lines found by Wood must be attributed to the large range covered by the concave grating. It is, however, questionable how ghosts and false lines in the spectra formed by a concave grating can be discriminated from true lines without some means of crossing them. We have no doubt that there is a group of satellites near the principal line as shown in Pl. I. fig. 1, in which the principal line appears on both sides, and the branches of the parabola on which the interference points lie run oblique to the echelon spectra, which are vertical. The arrangement of the satellites is shown in the diagram (fig. 1).

We believe that by crossing the concave-grating spectrum

with that given by the Lummer-Gehrcke plate, the confusion as to orders of spectra and the uncertainty as to the presence of ghosts can be easily avoided. Experiments in this direction are now in preparation. Crossed spectra obtained by the combination of a concave grating with a Fabry-Perot interferometer were utilized by Eversheim\* for the

Fig. 1.



Echelon and Lummer-Gehrcke Plate.

determination of wave-lengths, and by Wood† for the study of the band spectrum.

*Plane-parallel Plate and Air-Plate combined.*—The Fabry-Perot interferometer used in the present experiment was made by Hilger, and was of the sliding type; the air-plate had the range of 12 cm., one of the plates being movable by a screw, which was provided with a side micrometer for slow motion. The guide for displacing a half-silvered glass plate was nearly perfect, which is an essential quality for the work now under discussion.

Light from a monochromator passed through the air-plate and fell on a prism attached at one end of the plate for direct vision. By turning the plate so that the light fell at proper incidence, the interference points could be made to

\* Eversheim, *Ann. der Phys.* xxx. p. 815 (1909).

† Wood, *Phil. Mag.* xxvi. p. 176 (1913).



lie in horizontal rows and vertical columns. This is the most convenient position for observation. By adjusting the thickness of the air-plate, we can bring the interference points due to a special line, which we wish to study, in different positions with respect to the line of reference. This combination is sometimes convenient for determining a small difference in wave-lengths, for example, the relative position of satellites. The crossed spectra of the green line of mercury are shown in Pl. I. fig. 2. The fine structure of the line is apparent at a glance, and what is more interesting is the vagueness of the principal line, suggesting that there is a structure in it, as remarked by Janicki \*. The accompanying diagram shows the position of the satellites (fig. 2).

Fig. 2.



Lummer-Gehrcke Plate and Fabry-Perot Plate.

The different distributions of interference points by varying the thickness of air-plate present most interesting features; when the visual observation is possible, we can judge from the relative displacement of interference points the difference in wave-lengths, even if several orders of spectra are overlapped. The method of coincidence can be applied with more accuracy in the combination here described than with the Fabry-Perot interferometer only. From this practical point of view, the sliding interferometer

\* Janicki, *loc. cit.*

has an advantage over that with a fixed etalon. The order of accuracy with which we can find a small difference in wave-lengths is such that it is sometimes necessary to bring in the correction to the usual formula of reduction for the difference in the order of spectrum from that at grazing exit, although the observation is made very near it.

There is, however, one doubtful point which requires special mention. For observing the interference points distinctly, the objective of the telescope or photographic camera should not be focussed to infinity. This problem has been discussed by Kolaček \*, with results which make the application of the usual formula of reduction somewhat doubtful.

*Air-plate and Echelon Grating combined.*—The crossed spectra formed by this combination present special interest on account of the ease with which two spectrum lines can be brought into coincidence. The photograph of the green line with some of its satellites is shown in Pl. I. fig. 3; the principal line appears on both sides with nearly equal intensity. The arrangement of interference points is not so simple as with the combination before mentioned, but it has the advantage of facilitating the measurement of the difference in wave-lengths, so that it cannot be overlooked in spectrometry.

Denoting the distance between the plates in the interferometer by  $e$ , the order of interference for light of wave-length  $\lambda$  by  $P$ , which is an integer, generally very large, and calling the angle subtended by the ring  $2\theta$ , which is generally small, we have the relation

$$\frac{2e}{\lambda} \cos \theta = P.$$

Counting the rings from the centre, we have for the  $h$ th ring

$$P_h = \frac{2e}{\lambda} \cos \theta_h = P - h + 1.$$

If we determine the diameters of  $m$  different rings, we have

$$\sum_1^m P_h = mP - \frac{m(m-1)}{2} = \frac{2e}{\lambda} \sum_1^m \cos \theta_h.$$

Neglecting  $\theta^4$ , and putting

$$\frac{1}{2} \sum_1^m \theta_h^2 = \epsilon,$$

\* Kolaček, *Ann. der Phys.* xxxix. p. 1431 (1912).

132 Prof. Nagaoka and Mr. T. Takamine on *Crossed Spectra*  
which is known by observation,

$$\frac{\left(P - \frac{m-1}{2}\right)\lambda}{1 - \frac{\epsilon}{m}} = 2e.$$

If we make observations on lines of wave-lengths  $\lambda', \lambda'', \dots$ , we shall have similarly

$$2e = \frac{\left(P' - \frac{m'-1}{2}\right)\lambda'}{1 - \frac{\epsilon'}{m'}} = \frac{\left(P'' - \frac{m''-1}{2}\right)\lambda''}{1 - \frac{\epsilon''}{m''}} = \dots$$

Thus the difference between wave-lengths  $\lambda$  and  $\lambda'$  is

$$\delta\lambda = \lambda' - \lambda = \left( \frac{P' - \frac{m'-1}{2}}{1 - \frac{\epsilon'}{m'}} - \frac{P - \frac{m-1}{2}}{1 - \frac{\epsilon}{m}} \right) \frac{\lambda\lambda'}{2e}.$$

The expression simplifies for  $\frac{\epsilon}{m} = \frac{\epsilon'}{m'}$ ; when this condition is satisfied for  $m=m'$ , the rings due to  $\lambda$  and  $\lambda'$  must coincide.

The most favourable case is evidently  $P\frac{\epsilon}{m} = P'\frac{\epsilon'}{m'}$ , but we cannot always make the optical thickness of the air-plate fulfil this condition, so that there is usually a small residual. Putting  $\frac{\epsilon'}{m'} - \frac{\epsilon}{m} = \xi$ , and remembering that  $P' - P$  is usually small compared with  $P$  or  $P'$ ,

$$\delta\lambda = \left\{ (P' - P) \left( 1 + \frac{\epsilon}{m} \right) + P'\xi \right\} \frac{\lambda\lambda'}{2e}.$$

When  $\delta\lambda$  is approximately known, we may arrive at a more exact value by using crossed spectra, in which the above formula for  $\delta\lambda$  is practically utilized. For this purpose, it is in the first place necessary to have a line of standard wave-length, and to determine the zero-correction of the micrometer attached to the interferometer. As the screw is not generally free from periodic errors, the scale cannot be always relied upon, and one must have some means of checking the readings. This is easily done by using two neighbouring lines of mercury 5790 and 5769.

The difference in wave-lengths amounts to  $21.0609 \text{ \AA.U.}$  according to Fabry and Perot, and also by our measurements with crossed spectra, at  $15^\circ$  and 760 mm. pressure. The coincidence takes place at intervals of  $0.079317 \left(1 - \frac{\theta^2}{2}\right) \text{ mm.},$

and as it can be accurately observed, there is no difficulty in measuring the thickness of an air-plate to within a few microns. When the Fabry-Perot interferometer is used singly, the accuracy in deciding the exact coincidence of the two systems of rings is rather limited, even if these lines are sharp and pure. In case of mercury lines, the immersion of satellites on one side of the principal line causes an apparent shift of the principal to that side and causes illusion. But if we place another interference apparatus such as a Lummer-Gehrcke plate or an echelon grating, and open the slit widely so that the interference points, instead of being dots, are small portions of circular arcs, the coincidences are easier to observe, and we are free from the error caused by satellites. Knowing  $e$ , we can calculate  $P$  and  $P'$ , which are whole numbers. It must not, however, be forgotten that the optical thickness varies with wave-length, so that we cannot use the value of  $e$  found by the yellow lines for red or violet lines. According to Fabry and Perot, the difference in  $e$  amounts to a few millimicrons within the visible spectrum, so that by making the air-plate sufficiently thick, we can neglect this small difference in  $e$ .

Thus far the discussion does not differ much from the method introduced by Fabry and Perot, or that modified by Lord Rayleigh\* and others. The advantage of crossed spectra consists in the accuracy with which we can measure the position of interference points; consequently, the distance between the plates  $e$  and the values of  $\epsilon$  and  $\epsilon'$  are exactly known. This is due to the separate appearance of interference points for different lines, even in the position of coincidence in the rings, when observed with interferometer only. When the centre of the ring is known, the coordinates of the interference points will determine at once the values of  $\epsilon$  and  $\epsilon'$ . The coincidence of the rings observed with the interferometer only may be perfect, but on interposing the echelon, and measuring the numerous points, we generally find a slight deviation, which we can detect from the difference in the values of  $\epsilon$  and  $\epsilon'$ . So far as our experience goes, the position of the centre of the system of rings is more difficult to measure than the coordinates of interference

\* Rayleigh, *Phil. Mag.* xi. p. 685 (1906).



points. The accompanying figure gives the sketch of how the rings and the lines are superposed on coincidence. The coordinates may be utilized for deducing the position of the centre by the geometrical property of circle. A more practical way of finding it is to photograph a small portion of the system of rings after removing the echelon; this can be done in the arrangement of the apparatus constructed by Hilger.

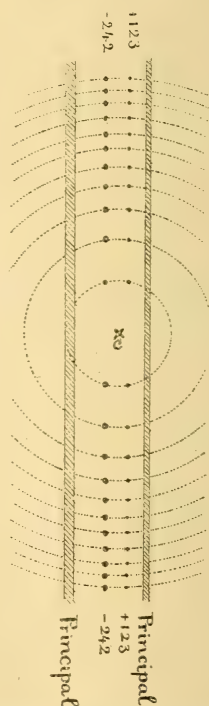
The method of procedure is as follows:—The apparatus is enclosed in a wooden box lined with thick cork plates, to avoid changes of temperature. The photographs of crossed spectra for the reference line and for the line in question are taken, the temperature and pressure of the air in the box being noted. Sometimes it will be necessary to note the hygrometric state also. Then  $x$ - and  $y$ -coordinates, of interference points, are measured by a delicate micrometer on the photographs. The position of the centre of the rings is determined from these values; thus  $\theta$ 's are easily calculated, and consequently

$\frac{\epsilon}{m}$  and  $\frac{\epsilon'}{m'}$  are known. Two trial experiments are sufficient to make

$\frac{\epsilon}{m}$  differ by less than one per cent. from  $\frac{\epsilon'}{m'}$ . As the temperature is generally changing slowly, it is necessary to measure  $e$  before and after the experiment.

We give an example of our determination of  $\delta\lambda$  made on the yellow lines of mercury and another on two satellites of the green line. As a reference line, we assumed the wave-length of the yellow line 5790.6593 according to Fabry and Perot, and that of the neighbouring line to be about 5769.698. These lines were photographed in crossed spectra of echelon and plate as in Pl. I. fig. 4. The temperature of the air was determined by means of Assmann's aspiration thermometer, which is indispensable for accurate works with air-plate, as a thermometer simply hung in the neighbourhood

Fig. 3.



Echelon and Fabry-Perot Plate.  
Coincidence of the Satellites  
+123 and -242.

of the interferometer does not indicate the true temperature of the air. The coordinates of interference points were read by means of a micrometer microscope detached from a geodetic comparator, one division of the drum being equivalent to  $1\mu$ , which reduced to angular measure in the focal plane of the photographic objective was equivalent to  $0''\cdot4623$ .

The following measurements were made for the difference in wave-lengths between the satellites  $-242$  and  $+123$  of the green line, the appearance of the nearly coincident points being given in Pl. I. fig. 3.

	$e$ .	$P' - P$ .	$(P' - P)\frac{\dot{e}}{m}$ .	$P'\xi$ .	$\delta\lambda$ .
Pl. No. 7...	49.081 mm.	12	(T)+0.00029 (N)+0.00029	+0.01468 +0.01851	365.0 m.Å.U. 365.1 „
Pl. No. 10...	49.085 mm.	12	(T)+0.00039 (N)+0.00039	+0.01320 +0.01581	364.9 „ 365.0 „
Pl. No. 21...	57.180 mm.	14	(T)+0.00012 (N)+0.00012	-0.00121 +0.00267	365.0 „ 365.1 „
Pl. No. 43...	57.161 mm.	14	(T)+0.00034 (N)+0.00034	-0.00320 -0.00255	365.1 „ 365.1 „

These measurements show that the first decimal place of m.Å.U. is generally reliable. By crossing the Lummer-Gehrcke plate with the Fabry-Perot interferometer, we found  $\delta\lambda = 364.4$  m.Å.U. for these two lines. The discrepancy between the two will have close connexion with the discussion raised by Kolačák already mentioned.

When  $P' - P$  is large more exact values can be obtained. The following example gives the difference in wave-lengths between the yellow lines of mercury :—

	$e$ .	$P' - P$ .	$\delta\lambda$ (Å.U.).
Pl. No. 72 .....	16.8194 mm.	212	(T) 21.0610
Pl. No. 92 .....	16.7364 mm.	211	(T) 21.0610 (N) 21.0605
Pl. No. 115 .....	48.9892 mm.	618	(T) 21.0610 (N) 21.0607
Pl. No. 117 .....	48.9894 mm.	618	(T) 21.0607 (N) 21.0611

The mean of these measurements is equal to 21·0609, exactly agreeing with the value found by Fabry and Perot.

It is to be remarked that we have here used only for convenience sake one of the yellow lines of mercury as a reference line; evidently the difference in wave-lengths can be easily referred to standard lines of cadmium. We believe that the present method can be applied to various other purposes of accurate spectroscopic work.

August 7, 1913.

XIII. *The Classification of Electromagnetic Fields.* By H. BATEMAN, M.A., Ph.D., Johnston Research Scholar, Johns Hopkins University\*.

§ 1. THE field of the two vectors  $E$ ,  $H$  will be called electromagnetic when Maxwell's equations

$$\left. \begin{aligned} \frac{\partial H_z}{\partial y} - \frac{\partial H_y}{\partial z} &= \frac{\partial E_x}{\partial t}, & \frac{\partial E_z}{\partial y} - \frac{\partial E_y}{\partial z} &= -\frac{\partial H_x}{\partial t}, \\ \dots & \dots & \dots & \dots \\ \frac{\partial E_x}{\partial x} + \frac{\partial E_y}{\partial y} + \frac{\partial E_z}{\partial z} &= 0, & \frac{\partial H_x}{\partial x} + \frac{\partial H_y}{\partial y} + \frac{\partial H_z}{\partial z} &= 0, \end{aligned} \right\} \quad (1)$$

are satisfied for some real domain of the variables  $x, y, z, t$ . In general these equations cannot be regarded as holding for all real values of  $x, y, z, t$ , and the exceptional space-time points or domains of such points are to be regarded as the singularities of the electromagnetic field †.

The simplest type of point singularity is one which moves with a velocity less than unity, along an arbitrary curve. If we solve equations (1) in the usual way with the aid of four potentials  $A_x, A_y, A_z, \Phi$  satisfying the wave-equation

$$\frac{\partial^2 \Omega}{\partial x^2} + \frac{\partial^2 \Omega}{\partial y^2} + \frac{\partial^2 \Omega}{\partial z^2} = \frac{\partial^2 \Omega}{\partial t^2}, \quad \dots \quad (2)$$

and the relations

$$\frac{\partial A_x}{\partial x} + \frac{\partial A_y}{\partial y} + \frac{\partial A_z}{\partial z} + \frac{\partial \Phi}{\partial t} = 0, \quad \dots \quad (3)$$

$$\frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z} = H_x, \quad \frac{\partial A_x}{\partial t} + \frac{\partial \Phi}{\partial x} = -E_x; \quad \dots \quad (4)$$

\* Communicated by the Author.

† We shall suppose that  $E_x, H_x$ , &c., are one-valued functions of  $x, y, z, t$  for the whole of the real domain of these variables, the point singularities being excluded.

an electromagnetic field with this simple type of singularity is obtained by putting

$$A_x = \frac{\xi'(\tau)}{M}, \quad A_y = \frac{\eta'(\tau)}{M}, \quad A_z = \frac{\rho'(\tau)}{M}, \quad \Phi = \frac{1}{M}, \quad (5)$$

where  $\tau$ ,  $M$  are defined by the equations

$$[x - \xi(\tau)]^2 + [y - \eta(\tau)]^2 + [z - \zeta(\tau)]^2 = (t - \tau)^2, \quad t \geq \tau, \quad (6)$$

$$\xi'^2(\tau) + \eta'^2(\tau) + \zeta'^2(\tau) < 1, \quad . \quad . \quad (7)$$

$$M = \xi'(\tau)[x - \xi] + \eta'(\tau)[y - \eta] + \zeta'(\tau)[z - \zeta] - (t - \tau). \quad (8)$$

If all these conditions are satisfied, there is only one value of  $\tau$  for each point  $(x, y, z, t)$ , and  $M$  only vanishes when all the terms in (6) are zero, *i. e.* when  $x, y, z, t$  coincides with the moving-point  $(\xi, \eta, \zeta)^*$ . This electromagnetic field, which was discovered by Liénard, is rightly regarded as being of fundamental importance in the electron theory of matter, and electromagnetic fields which can be obtained by superposing a number of fields of this simple type are studied almost exclusively.

For the sake of thoroughness, however, it is desirable that all types of electromagnetic fields should be studied, the aim being, if possible, to discover a number of fundamental types from which all real electromagnetic fields can be derived by superposition †.

§ 2. Solutions analogous to Liénard's may be obtained by discarding the inequality (7), or by considering complex functions  $\xi, \eta, \zeta$  and a complex variable  $\tau$ , or, finally, by putting

$$A_x = \Sigma \pm \frac{\xi'(u)}{M}, \quad A_y = \Sigma \pm \frac{\eta'(u)}{M}, \quad A_z = \Sigma \pm \frac{\zeta'(u)}{M}, \quad \Phi = 0, \quad (9)$$

where the summation extends over values of  $u$  for which ‡

$$[x - \xi(u)]^2 + [y - \eta(u)]^2 + [z - \zeta(u)]^2 = t^2, \quad . \quad (10)$$

$$\text{and} \quad M = \xi'(u)[x - \xi] + \eta'(u)[y - \eta] + \zeta'(u)[z - \zeta]. \quad (11)$$

In the first case the singularity  $(\xi, \eta, \zeta, \tau)$  travels with a

\* For further details, see Schott's 'Electromagnetic Radiation.'

† Differentiations with regard to the variables  $x, y, z, t$  are supposed to be included, as well as integrations with regard to variable parameters.

‡ Any finite number of roots may be chosen and the signs in (9) distributed arbitrarily and Maxwell's equations will be satisfied. In making a choice of the roots and signs we must endeavour to make the components of  $E$  and  $H$  single-valued functions of  $x, y, z, t$ .



velocity greater than or equal to that of light. This case has been discussed at some length by Sommerfeld and Schott (*l. c.*). In the case of the electromagnetic field defined by the potentials (9) there are primary singularities distributed along the curve  $x=\xi(u)$ ,  $y=\eta(u)$ ,  $z=\zeta(u)$  at time  $t=0$ , and these give rise to secondary singularities which at time  $t$  lie on a tubular surface having the given curve as axis. If we write  $x-a$ ,  $y-b$ ,  $z-c$ ,  $t-\tau$  in place of  $x$ ,  $y$ ,  $z$ ,  $t$ , and integrate over a suitable domain of the variables  $a$ ,  $b$ ,  $c$ ,  $\tau$ , we may get rid of the awkward infinities of the electric and magnetic vectors, but the derivatives of these vectors will not all be continuous over the regions occupied by these infinities. The chief peculiarity of an electromagnetic field of this kind is that a portion of matter sends out radiations for a finite interval of time, and the radiations, which seem to be partly of a material nature, travel outwards with the velocity of light. The radiated matter, however, seems generally to fill the spaces between a number of pairs of moving surfaces, and so the present type of electromagnetic field is essentially different from any of the fields which have so far been observed in nature.

An electromagnetic field of a more promising nature is obtained by writing

$$A_x = \sum \frac{l(u)}{w}, \quad A_y = \sum \frac{m(u)}{w}, \quad A_z = \sum \frac{n(u)}{w}, \quad \Phi = \sum \frac{1}{w}, \quad . \quad (12)$$

where the summation extends over some of the values of  $u$  for which equation (10) is satisfied and

$$l^2 + m^2 + n^2 = 1, \quad . \quad . \quad . \quad . \quad (13)$$

$$l\xi' + my' + n\zeta' = 0, \quad . \quad . \quad . \quad . \quad (14)$$

$$w = l(x - \xi) + m(y - \eta) + n(z - \zeta) - t. \quad . \quad . \quad (15)$$

If  $l$ ,  $m$ ,  $n$  are real, the quantity  $w$  vanishes only when

$$\frac{x - \xi}{l} = \frac{y - \eta}{m} = \frac{z - \zeta}{n} = \frac{t}{1}. \quad . \quad . \quad . \quad (16)$$

The singularities of the electromagnetic field may be described by saying that there are guns distributed along the curve

$$x = \xi(u), \quad y = \eta(u), \quad z = \zeta(u). \quad . \quad . \quad . \quad (17)$$

Each gun points in a direction at right angles to the curve, and fires out a singularity or bullet at time  $t=0$ . The bullets all move in straight lines with the velocity of light.

This type of electromagnetic field may be generalized by integration just like the previous one. In the resulting electromagnetic field material particles are fired out from a material wire for a certain interval of time, and these particles move along straight lines with the velocity of light. The way in which the shape and size of such a particle varies during its motion has not yet been ascertained.

§ 3. We shall now discuss another class of electromagnetic fields in which the radiated energy is concentrated round certain moving points which travel with the speed of light, but in this case the difficulty with regard to the roots of (10) is absent.

Defining  $\tau$  as before by means of equations (6) and (7), we choose 16 functions of  $\tau$  which satisfy the equations

$$\left. \begin{aligned} l^2 + m^2 + n^2 &= p^2, & l_0^2 + m_0^2 + n_0^2 &= p_0^2, & \lambda^2 + \mu^2 + \nu^2 &= \varpi^2, \\ \lambda_0^2 + \mu_0^2 + \nu_0^2 &= \varpi_0^2, \end{aligned} \right\} \quad (18)$$

$$\left. \begin{aligned} l\lambda + m\mu + n\nu &= p\varpi, & l_0\lambda + m_0\mu + n_0\nu &= p_0\varpi, & l\lambda_0 + m\mu_0 + n\nu_0 &= p\varpi_0, \\ l_0\lambda_0 + m_0\mu_0 + n_0\nu_0 &= p_0\varpi_0; \end{aligned} \right\} \quad (19)$$

and write

$$\left. \begin{aligned} w &= l(x-\xi) + m(y-\eta) + n(z-\zeta) - p(t-\tau), \\ w_0 &= l_0(x-\xi) + m_0(y-\eta) + n_0(z-\zeta) - p_0(t-\tau), \\ \sigma &= \lambda(x-\xi) + \mu(y-\eta) + \nu(z-\zeta) - \varpi(t-\tau), \\ \sigma_0 &= \lambda_0(x-\xi) + \mu_0(y-\eta) + \nu_0(z-\zeta) - \varpi_0(t-\tau). \end{aligned} \right\} \quad (20)$$

If  $M$  is defined by equation (8), it is easy to prove that when  $f$  and  $F$  are arbitrary functions the expressions

$$\Omega = \frac{1}{M} f\left(\frac{\sigma}{w}, \tau\right), \quad \Omega_0 = \frac{1}{M} F\left(\frac{\sigma}{w_0}, \tau\right) \quad (21)$$

satisfy the wave-equation (2), and that the potentials

$$\left. \begin{aligned} A_x &= \frac{l}{M} \frac{\sigma}{w} + \frac{l_0}{M} \frac{\sigma}{w_0} - \frac{2\lambda}{M}, & A_y &= \frac{m}{M} \frac{\sigma}{w} + \frac{m_0}{M} \frac{\sigma}{w_0} - \frac{2\mu}{M}, \\ A_z &= \frac{n}{M} \frac{\sigma}{w} + \frac{n_0}{M} \frac{\sigma}{w_0} - \frac{2\nu}{M}, & \Phi &= \frac{p}{M} \frac{\sigma}{w} + \frac{p_0}{M} \frac{\sigma}{w_0} - \frac{2\varpi}{M}, \end{aligned} \right\} \quad (22)$$

which consequently satisfy (2), are connected by the relation (3).

The electromagnetic field specified by these potentials has singularities at space-time points for which  $\sigma_0$  is zero. To

see this we remark that there is a relation of the form

$$\sigma\sigma_0 = \theta w w_0, \quad . \quad . \quad . \quad . \quad . \quad (23)$$

where  $\theta$  is some function of  $\tau$ . The existence of a relation of this type is easily realized by considering the particular case when  $p_0 = p$ ,  $\varpi_0 = \varpi$ , and

$$\left. \begin{aligned} \lambda &= \frac{p\varpi}{q}, & \mu &= 0, & \nu &= \frac{\varpi}{q} \sqrt{q^2 - p^2}; \\ \lambda_0 &= \frac{p\varpi}{q}, & \mu_0 &= 0, & \nu_0 &= -\frac{\varpi}{q} \sqrt{q^2 - p^2}; \\ l &= q, & m &= \sqrt{p^2 - q^2}, & n &= 0; \\ l_0 &= q, & m_0 &= -\sqrt{p^2 - q^2}, & n_0 &= 0. \end{aligned} \right\} \quad (24)$$

The relation (23) is then verified at once by using (6).

Since the general values of  $\lambda$ ,  $\mu$ ,  $\nu$ , &c., may be derived from these particular ones by a suitable orthogonal substitution, it is easy to see that a relation of type (23) holds universally.

We shall now assume that  $\lambda$ ,  $\mu$ ,  $\nu$ ,  $\varpi$ ,  $\lambda_0$ ,  $\mu_0$ ,  $\nu_0$ ,  $\varpi_0$  are all real, then it is easily seen that  $\sigma_0$  is zero when

$$\frac{x - \xi}{\lambda_0} = \frac{y - \eta}{\mu_0} = \frac{z - \zeta}{\nu_0} = \frac{t - \tau}{\varpi_0}.$$

Hence the electromagnetic field has a singularity which starts from the point  $(\xi, \eta, \zeta, \tau)$  and moves with the speed of light along a straight line whose direction cosines are proportional to  $(\lambda_0, \mu_0, \nu_0)$ . Taking each point  $(\xi, \eta, \zeta, \tau)$  in turn, we obtain all the singularities of the field in this way. The moving point  $(\xi, \eta, \zeta, \tau)$  may be described as a *gun* which moves about in an arbitrary prescribed manner and fires out "bullets" which travel with the speed of light. The direction in which the gun points at any instant can be chosen arbitrarily provided the differential coefficients of the functions  $\lambda$ ,  $\mu$ ,  $\nu$  . . . are continuous.

After a long calculation we find that the component of the electric force along the radius from  $(\xi, \eta, \zeta, \tau)$  to the point  $(x, y, z, t)$  at which the force is required is

$$\frac{2}{M^2} (\lambda \xi' + \mu \eta' + \nu \zeta' - \varpi) - \frac{\sigma \rho}{M^2 w} - \frac{\sigma \rho_0}{M^2 w_0},$$

where

$$\begin{aligned} \rho &= l \xi' + m \eta' + n \zeta' - p, \\ \rho_0 &= l_0 \xi' + m_0 \eta' + n_0 \zeta' - p_0. \end{aligned}$$

We shall assume that  $\rho$  and  $\rho_0$  vanish so that our expression may be finite for  $\sigma_0=0$ .

Integrating over the surface of a sphere for which  $t-\tau$  is constant, we find that the total charge associated with the singularity  $(\xi, \eta, \zeta, \tau)$  is

$$8\pi \cdot \frac{\lambda\xi' + \mu\eta' + \nu\zeta' - \varpi}{1 - \xi'^2 - \eta'^2 - \zeta'^2}.$$

In general the charge varies with  $\tau$ : to make it constant we must introduce a restriction such as

$$\lambda\xi' + \mu\eta' + \nu\zeta' - \varpi = \xi'^2 + \eta'^2 + \zeta'^2 - 1. \quad . \quad . \quad (25)$$

If, in particular, we take  $\varpi=1$ , this condition implies that the angle between the direction of the gun and the direction of the gun's motion has a cosine equal to  $v$ , where  $v$  is the velocity of the gun. We may get rid of the charge at the singularity  $(\xi, \eta, \zeta, \tau)$  by adding suitable multiples of Liénard's potentials ( $\delta$ ). To simplify our expressions, we shall add to (19) the additional equations

$$\varpi = \varpi_0 = p = p_0 = 1, \quad l\xi' + m\eta' + n\zeta' = 1, \quad l_0\xi' + m_0\eta' + n_0\zeta' = 1, \quad . \quad . \quad (26)$$

which, together with (19), lead to (25). The electromagnetic field specified by the potentials

$$\left. \begin{aligned} A_x &= \frac{l}{2M} \frac{\sigma}{w} + \frac{l_0}{2M} \frac{\sigma}{w_0} - \frac{\lambda - \xi'}{M}, \\ A_y &= \frac{m}{2M} \frac{\sigma}{w} + \frac{m_0}{2M} \frac{\sigma}{w_0} - \frac{\mu - \eta'}{M}, \\ A_z &= \frac{n}{2M} \frac{\sigma}{w} + \frac{n_0}{2M} \frac{\sigma}{w_0} - \frac{\nu - \zeta'}{M}, \\ \Phi &= \frac{1}{2M} \left( \frac{\sigma}{w} + \frac{\sigma}{w_0} \right), \end{aligned} \right\} \quad . \quad . \quad (27)$$

then has no charge associated with the singularity  $(\xi, \eta, \zeta, \tau)$ . and both the electric and magnetic forces at  $(x, y, z, t)$  are perpendicular to the radius from  $(\xi, \eta, \zeta, \tau)$ .

If we add to (27) the field specified by the potentials

$$\left. \begin{aligned} A_x' &= \frac{l}{2M} \frac{\sigma_0}{w} + \frac{l_0}{2M} \frac{\sigma_0}{w_0} - \frac{\lambda_0 - \xi'}{M}, \\ A_y' &= \frac{m}{2M} \frac{\sigma_0}{w} + \frac{m_0}{2M} \frac{\sigma_0}{w_0} - \frac{\mu_0 - \eta'}{M}, \\ A_z' &= \frac{n}{2M} \frac{\sigma_0}{w} + \frac{n_0}{2M} \frac{\sigma_0}{w_0} - \frac{\nu_0 - \zeta'}{M}, \\ \Phi' &= \frac{1}{2M} \left( \frac{\sigma_0}{w} + \frac{\sigma_0}{w_0} \right), \end{aligned} \right\} \quad . \quad (28)$$



and make use of the relations

$$\lambda + \lambda_0 = 2\xi', \quad \mu + \mu_0 = 2\eta', \quad \nu + \nu_0 = 2\zeta', \quad \sigma + \sigma_0 = 2M, \quad (29)$$

we obtain the field specified by the potentials

$$\left. \begin{aligned} a_x &= \frac{l}{w} + \frac{l_0}{w_0}, & a_y &= \frac{m}{w} + \frac{m_0}{w_0}, \\ a_z &= \frac{n}{w} + \frac{n_0}{w_0}, & \phi &= \frac{1}{w} + \frac{1}{w_0}. \end{aligned} \right\} \quad (30)$$

The properties of this type of electromagnetic field have been discussed in a previous paper\*.

When  $w, w_0, \sigma, \sigma_0$  are defined by equations (19) the electromagnetic field specified by the potentials

$$\left. \begin{aligned} iA_x &= \frac{l}{M} \frac{\sigma}{w} - \frac{l_0}{M} \frac{\sigma}{w_0}, & iA_y &= \frac{m}{M} \frac{\sigma}{w} - \frac{m_0}{M} \frac{\sigma}{w_0}, \\ iA_z &= \frac{n}{M} \frac{\sigma}{w} - \frac{n_0}{M} \frac{\sigma}{w_0}, & i\Phi &= \frac{p}{M} \frac{\sigma}{w} - \frac{p_0}{M} \frac{\sigma}{w_0}, \end{aligned} \right\} \quad (31)$$

has singularities at points for which  $\sigma_0$  is zero and the electric charge associated with the point  $(\xi, \eta, \zeta, \tau)$  is zero. If in addition equations (26) are satisfied and we add to the potentials (31), the corresponding ones in which  $\sigma$  is replaced by  $\sigma_0$ , we obtain the potentials

$$\left. \begin{aligned} ia_x &= \frac{l}{w} - \frac{l_0}{w_0}, & ia_y &= \frac{m}{w} - \frac{m_0}{w_0}, & ia_z &= \frac{n}{w} - \frac{n_0}{w_0}, \\ \phi &= \frac{1}{w} - \frac{1}{w_0}, \end{aligned} \right\} \quad (32)$$

These specify an electromagnetic field in which both the electric and magnetic forces at  $(x, y, z, t)$  are perpendicular to the radius from  $\xi, \eta, \zeta, \tau$ . The field has singularities at points where  $w$  and  $w_0$ , and consequently  $\sigma$  or  $\sigma_0$ , are zero. The moving point  $\xi, \eta, \zeta, \tau$  may be described as a gun which fires out magnetic doublets in directions for which  $\sigma$  and  $\sigma_0$  vanish respectively. If we write

$$\frac{x - \xi}{t - \tau} = \alpha, \quad \frac{y - \eta}{t - \tau} = \beta, \quad \frac{z - \zeta}{t - \tau} = \gamma,$$

and treat  $\alpha, \beta, \gamma$  as constants, the components of the electric

\* Phil. Mag. Oct. 1913.

and magnetic vectors may be expressed in the forms

$$\left. \begin{aligned} iE_x &= \frac{1}{M} \frac{d}{d\tau} \left[ \frac{l-\alpha}{l\alpha+m\beta+n\gamma-1} - \frac{l_0-\alpha}{l_0\alpha+m_0\beta+n_0\gamma-1} \right], \\ &= \frac{i}{M} \frac{d}{d\tau} \left[ \frac{\nu\beta-\mu\gamma}{\lambda\alpha+\mu\beta+\nu\gamma-1} - \frac{\nu_0\beta-\mu_0\gamma}{\lambda_0\alpha+\mu_0\beta+\nu_0\gamma-1} \right], \\ iH_x &= \frac{1}{M} \frac{d}{d\tau} \left[ \frac{\beta n-\gamma m}{l\alpha+m\beta+n\gamma-1} - \frac{\beta n_0-\gamma m_0}{l_0\alpha+m_0\beta+n_0\gamma-1} \right], \\ &= -\frac{i}{M} \frac{d}{d\tau} \left[ \frac{\lambda-\alpha}{\lambda\alpha+\mu\beta+\nu\gamma-1} - \frac{\lambda_0-\alpha}{\lambda_0\alpha+\mu_0\beta+\nu_0\gamma-1} \right]. \end{aligned} \right\} \quad (33)$$

With the aid of these expressions we can show that the lines of electric and magnetic force on a sphere whose centre is at  $(\xi, \eta, \zeta, \tau)$  are such that when the sphere is inverted into a plane the electric lines of force are represented by the equipotential lines due to two doublets, and the magnetic lines of force by the corresponding stream lines, the flow being in two dimensions. The bullets are thus magnetic doublets.

§4. A very general type of electromagnetic field in which the electric and magnetic forces at  $x, y, z, t$  are perpendicular to the radius from  $\xi, \eta, \zeta, \tau$  may be obtained as follows:—

Let  $w, w_0, \sigma$  be defined by equations (20) and write

$$\begin{aligned} \theta &= f\left(\frac{\sigma}{w}, \tau\right) + f\left(\frac{\sigma}{w_0}, \tau\right), \\ \left. \begin{aligned} H_x &= \frac{\partial(\theta, \tau)}{\partial(y, z)}, & H_y &= \frac{\partial(\theta, \tau)}{\partial(z, x)}, & H_z &= \frac{\partial(\theta, \tau)}{\partial(x, y)}; \\ E_x &= \frac{\partial(\theta, \tau)}{\partial(x, t)}, & E_y &= \frac{\partial(\theta, \tau)}{\partial(y, t)}, & E_z &= \frac{\partial(\theta, \tau)}{\partial(z, t)}. \end{aligned} \right\} \quad (34) \end{aligned}$$

Then, if

$$iv = f\left(\frac{\sigma}{w}, \tau\right) - f\left(\frac{\sigma}{w_0}, \tau\right),$$

we have also

$$\left. \begin{aligned} H_x &= -\frac{\partial(\nu, \tau)}{\partial(x, t)}, & H_y &= -\frac{\partial(\nu, \tau)}{\partial(y, t)}, & H_z &= -\frac{\partial(\nu, \tau)}{\partial(z, t)}; \\ E_x &= \frac{\partial(\nu, \tau)}{\partial(y, z)}, & E_y &= \frac{\partial(\nu, \tau)}{\partial(z, x)}, & E_z &= \frac{\partial(\nu, \tau)}{\partial(x, y)} \end{aligned} \right\} \quad (35)$$

and it is evident from these two sets of relations that Maxwell's equations (1) are satisfied.

To verify these identities we have to show that if

$$s = \theta + iv = 2f\left(\frac{\sigma}{w}, \tau\right),$$

$$\frac{\partial(s, \tau)}{\partial(y, z)} = i \frac{\partial(s, \tau)}{\partial(x, t)}, \quad \frac{\partial(s, \tau)}{\partial(z, x)} = i \frac{\partial(s, \tau)}{\partial(y, t)}, \quad \frac{\partial(s, \tau)}{\partial(x, y)} = i \frac{\partial(s, \tau)}{\partial(z, t)}. \quad (36)$$

Now we find at once that

$$\left(\frac{\partial s}{\partial x}\right)^2 + \left(\frac{\partial s}{\partial y}\right)^2 + \left(\frac{\partial s}{\partial z}\right)^2 = \left(\frac{\partial s}{\partial t}\right)^2,$$

$$\frac{\partial s}{\partial x} \frac{\partial \tau}{\partial x} + \frac{\partial s}{\partial y} \frac{\partial \tau}{\partial y} + \frac{\partial s}{\partial z} \frac{\partial \tau}{\partial z} = \frac{\partial s}{\partial t} \frac{\partial \tau}{\partial t},$$

$$\left(\frac{\partial \tau}{\partial x}\right)^2 + \left(\frac{\partial \tau}{\partial y}\right)^2 + \left(\frac{\partial \tau}{\partial z}\right)^2 = \left(\frac{\partial \tau}{\partial t}\right)^2,$$

$$\therefore \frac{\partial s}{\partial x} \cdot \frac{\partial(s, \tau)}{\partial(x, t)} + \frac{\partial s}{\partial y} \cdot \frac{\partial(s, \tau)}{\partial(y, t)} + \frac{\partial s}{\partial z} \cdot \frac{\partial(s, \tau)}{\partial(z, t)} = 0,$$

$$\frac{\partial \tau}{\partial x} \cdot \frac{\partial(s, \tau)}{\partial(x, t)} + \frac{\partial \tau}{\partial y} \cdot \frac{\partial(s, \tau)}{\partial(y, t)} + \frac{\partial \tau}{\partial z} \cdot \frac{\partial(s, \tau)}{\partial(z, t)} = 0.$$

Hence it will be sufficient to verify the first of the equations (36). To do this we must show that

$$\left(\mu \frac{\partial \tau}{\partial z} - \nu \frac{\partial \tau}{\partial y} - i\lambda \frac{\partial \tau}{\partial t} - i\omega \frac{\partial \tau}{\partial x}\right)w = \left(m \frac{\partial \tau}{\partial z} - n \frac{\partial \tau}{\partial y} - il \frac{\partial \tau}{\partial t} - ip \frac{\partial \tau}{\partial x}\right).$$

If now we use the values (24) this relation is easily seen to be satisfied in virtue of (6). We may infer, then, that it is satisfied in the general case.

In the electromagnetic field (34) the electric and magnetic forces at  $(x, y, z, t)$  are at right angles to the radius from  $(\xi, \eta, \zeta, \tau)$ ; they are also at right angles to one another and equal in magnitude. The moving point  $(\xi, \eta, \zeta, \tau)$  again has the character of a gun which fires out bullets which move with the speed of light and are singularities of the electromagnetic field.

The lines of electric and magnetic force on a sphere whose centre is the point  $(\xi, \eta, \zeta, \tau)$  are easily drawn. It follows at once from (34) and (35) that the magnetic lines of force are given by  $\theta = \text{constant}$  and the electric lines of force by

$\nu = \text{constant}$ . By choosing the function  $f\left(\frac{\sigma}{w}, \tau\right)$  in a suitable

way we can make the distribution of the lines of force satisfy certain prescribed conditions.

§5. The electromagnetic fields of sections 3 and 4 may evidently be generalized by writing  $x+a$ ,  $y+b$ ,  $z+c$ ,  $t+\epsilon$  in place of  $x$ ,  $y$ ,  $z$ ,  $t$  and integrating over some domain of the point  $(a, b, c, \epsilon)$ . It should be possible in this way to get rid of the point singularities and replace them by material particles throughout which the electric and magnetic forces are finite, but do not necessarily satisfy Maxwell's equations.

The electromagnetic fields of sections 3 and 4 may also be generalized by adopting the method of section 2, but the analysis is not of sufficient interest to be given in detail.

The discussion of the singularities which has been given here is not exhaustive, for we have omitted the case of moving singularities at infinity; the fields which are obtained in this way, however, may be regarded as limiting cases of those which have already been discussed. The case of a primary singularity which moves with a velocity greater than that of light has been mentioned only very briefly. The investigation given in Schott's 'Electromagnetic Radiation' will give an idea of what is to be expected in this case.

Summing up the results of our investigations we are able to enumerate four distinct types of elementary electromagnetic fields.

In a field of the first type there is one point singularity which moves with a velocity less than that of light, and a constant electric charge is associated with the singularity. An electromagnetic field which can be obtained by superposing elementary fields of the first type will be said to belong to class A. We shall include under class A' fields which can be obtained by superposing the fields due to Hertzian oscillators in motion, an elementary field of this type being represented by the potentials \*

$$A = \text{curl } \Gamma - \frac{\partial \Omega}{\partial t} + \text{grad } \Psi, \quad \Phi = \text{div } \Omega - \frac{\partial \Psi}{\partial t}, \quad (37)$$

where the vectors  $\Gamma$ ,  $\Omega$  and the scalar  $\Psi$  are functions of the type  $\frac{f(\tau)}{M}$ ,  $\tau$  and  $M$  having the same meaning as in §1.

It is probable that all fields of class A' can be regarded as belonging to class A.

In a field of the second type there is a point singularity (the gun) which moves with a velocity less than that of light, and point singularities are fired out from the gun with

\* These are immediate generalizations of the potentials used by Prof. E. T. Whittaker, Proc. London Math. Soc. ser. 2, vol. i. (1903).



velocities equal to that of light, an electromagnetic field which is built up from elementary fields of this type will be said to belong to class B.

In a field of the third type the primary singularities lie along a curve at some instant  $\tau$ , at any subsequent time there are singularities distributed all over a tubular surface having the curve as axis. An electromagnetic field which is built up from elementary fields of this type will be said to belong to class C.

In a field of the fourth type the primary singularity moves with a velocity which is sometimes (or always) greater than that of light, and secondary singularities are fired out in various directions with the velocity of light. An electromagnetic field which is built up from elementary fields of this type will be said to belong to class D.

It is possible that all these different types of electromagnetic fields can be obtained from a single fundamental type by superposition. The fundamental solution of the equation of wave-motion which seems to be the most suitable for such a purpose is of the form

$$\Omega = \frac{1}{(x-a)^2 + (y-b)^2 + (z-c)^2 - (t-\epsilon)^2} \times \int \left[ \frac{\lambda(x-a) + \mu(y-b) + \nu(z-c) - \varpi(t-\epsilon)}{l(x-a) + m(y-b) + n(z-c) - p(t-\epsilon)} \right], \quad (38)$$

where  $a, b, c, \epsilon, l, m, n, p, \lambda, \mu, \nu, \varpi$  are constants satisfying equations (18) and (19). To obtain from this a solution of the form (21) we must either regard  $a, b, c$  as functions of the complex variable  $\epsilon$  and integrate round a closed contour in the complex plane\*, or else regard  $a, b, c$  as functions of the real variable  $\epsilon$  and take the principal value of an integral. The difficulties of the analysis are, however, so great that it seems better to retain the four different classes of fields with the understanding that it may be necessary to supplement them.

When the list is complete any real field which can be derived by superposition from potentials of type (38) and which is such that the electric and magnetic forces never become infinite (although they may not satisfy Maxwell's equations over the whole domain of the real variables  $x, y, z, t$ ), ought to be obtainable by superposition from fields belonging to the different classes. A question which

\* This method has been used by Prof. A. W. Conway to obtain Liénard's potentials. Proc. London Math. Soc. ser. 2, vol. i.

will then have to be settled is that of the uniqueness of the representation. It seems likely that there is only one set of elementary fields which, when added together, will be equivalent to a given electromagnetic field for the whole domain of the real variables  $x, y, z, t$ , but this proposition evidently requires proof.

A further difficulty arises from the fact that we can find wave-functions which are homogeneous functions of degree  $n$  in  $x-a, y-b, z-c, t-\epsilon$ , where  $n$  is not an integer. There are also many valued wave-functions such as  $\tan^{-1} \frac{y}{x}$ .

Electromagnetic fields in which the components of  $\mathbf{E}$  and  $\mathbf{H}$  are represented by wave-functions of this type are, however, excluded by the condition, stated at the outset, that the components of  $\mathbf{E}$  and  $\mathbf{H}$  must be one-valued functions of  $x, y, z, t$  for the whole real domain of these variables.

XIV. *On the Action of a disturbing Force in the restricted Problem of Three Bodies.* By R. J. ПОСЛОК, B.A., B.Sc., Queen's College, Oxford\*.

IN the restricted problem of three bodies, let  $\mathbf{H}, \mathbf{J}$  represent the two larger bodies,  $\mathbf{P}$  the particle. Let  $\mathbf{J}$  be of mass unity,  $\mathbf{H}$  of mass  $\nu$ , and take  $\mathbf{HJ}$  as unit distance. Let  $n$  be the mean angular velocity of  $\mathbf{J}$ ;  $r, \rho$  the bipolar co-ordinates of  $\mathbf{P}$  referred to  $\mathbf{H}$  and  $\mathbf{J}$ . Then with reference to  $\mathbf{HJ}$  and a perpendicular thereto through the C.G. of  $\mathbf{H}$  &  $\mathbf{J}$  as moving axes rotating with angular velocity  $n$ , we have the equations

$$\left. \begin{aligned} \ddot{x} - 2 \cdot n \cdot \dot{y} &= \frac{\partial \Omega}{\partial x} \\ \ddot{y} + 2 \cdot n \cdot \dot{x} &= \frac{\partial \Omega}{\partial y} \end{aligned} \right\} \quad n^2 = \nu + 1,$$

$$2\Omega = \nu \left( r^2 + \frac{2}{r} \right) + \rho^2 + \frac{2}{\rho}; \quad r^2 = x^2 + y^2; \quad \rho^2 = (x-1)^2 + y^2.$$

These equations admit of Jacobi's integral, viz. :

$$V^2 = \dot{x}^2 + \dot{y}^2 = 2\Omega - C,$$

where  $V$  denotes the velocity of  $\mathbf{P}$  and  $C$  is a constant.

2. Let us now suppose that an additional body  $\mathbf{S}$  of mass  $\mu$  is introduced into the system. It is assumed that  $\mathbf{S}$  is small

\* Communicated by the Author.

enough or distant enough for us to be able to neglect its differential effect on H and J. Let  $SP = \sigma$ .

Jacobi's integral will, in general, no longer exist; though the equations will be of the same form provided we introduce into the function  $\Omega$  an additional term  $\frac{\mu}{\sigma}$ ; where  $\sigma$ , however, is an explicit function of the time  $t$ .

3. Confining ourselves as usual to two dimensional motion, two cases may arise in which the integral will still exist.

(i.) There may be a number of disturbing bodies so related that the time disappears from the function  $\Omega$ , *e. g.*, the bodies might be distributed in a circular belt with centre at the origin such that the density at any point was independent of the vectorial angle (though it might be a function of the radius vector). The minor planets and Saturn's rings might be very approximately represented by such a distribution.

(ii.) The disturbing body, or bodies, might be at rest relative to the rotating axes. Such will be the case when bodies are placed at the points of zero force, and will hold approximately of bodies oscillating near these points. We have examples of such in the Jupiter groups, Hector, Patroclus, &c.

In either of these cases the curves of zero velocity will be given by the equation  $2\Omega = C$  where  $C$  is an absolute constant, and

$$2\Omega = \nu \left( r^2 + \frac{2}{r} \right) + \rho^2 + \frac{2}{\rho} + \frac{2\mu}{\sigma}.$$

4. In the more general case, however, this integral will not exist. Assuming, however, that the disturbing force is not considerable, we may assume the integral  $V^2 = 2\Omega - C$  where  $C$  is no longer constant, but a function of the time  $t$ .

At any given time  $t$  the instantaneous curves of zero velocity will be given by  $2\Omega = C$ .

5. In the restricted problem of three bodies there exist certain forms of stable motion, such for instance as that in which P, if once an inferior planet, must always remain so. In such a case the curves of zero velocity consist in two closed ovals surrounding H and J. When a small disturbing force acts these ovals will swell and shrink periodically. Suppose for example that the disturbing force is due to the attraction of a planet S superior to J. We are

not concerned with the actual path of S provided its perihelion distance is greater than unity, and its differential effect on H and J is small. It may happen that the two oval curves never quite coalesce during the period of the disturbing force. In this case, although there is no fixed curve of zero velocity, the particle once started as an inferior planet must always remain so. The limits of the initial values of C will not be the same as in the case when S is non-existent. In order to find these values we must suppose that when S is at perihelion P is at the critical point between H and J; this is the most favourable case for disturbing the stability of the motion. If  $C_0$  denotes the critical value of C for undisturbed motion and  $SP = \sigma$ , we have as the criterion for stability  $C_0 < C - \frac{2\mu}{\sigma}$ ,

$$i. e. \quad C > C_0 + \frac{2\mu}{\sigma}.$$

We may at once extend the theorem to any number of disturbing planets and we have

$$C > C_0 + \frac{2\mu_1}{\sigma_1} + \frac{2\mu_2}{\sigma_2} + \dots$$

6. If the disturbing body is inferior to J we have only to treat J as the disturbing body and H and S as the two principal bodies. Similarly we may deal with cases in which P moves as a J satellite or as a planet superior to J or in which interchange between two forms is possible. We may introduce as many disturbing bodies as we please; it is only necessary to know in each case either the perihelion or the aphelion distance, and there is no difficulty in determining numerical limits for the initial value of C.

7. In the restricted problem of three bodies there exist certain points at which P can remain in relative equilibrium, three on the line HJ, and two at the apices of the equilateral triangles described on HJ. Let L denote one of these points. In the case of disturbed motion the actual critical point L' will lie near L, and will not be fixed. For example, if the disturbing force is due to a single superior planet S, L' will describe a small closed periodic curve round L.

8. In the case of three bodies it is known that the motion near such a point L on the line HJ is given by the



equations \*

$$\xi = h \cdot \cosh \alpha t + k \cdot \sinh \alpha t + H \cdot \cos \beta t + K \cdot \sin \beta t,$$

$$\eta = \frac{\alpha^2 - \gamma^2}{2n\alpha} (h \cdot \sinh \alpha t + k \cdot \cosh \alpha t) - \frac{\beta^2 + \gamma^2}{2n\beta} (H \cdot \sin \beta t - K \cdot \cos \beta t),$$

where  $\alpha, \beta, \gamma$  are numerical constants,  $h, k, H, K$ , depend on the initial conditions, and  $L$  is the origin of co-ordinates.

9. In the case of disturbed motion we may assume these same equations where  $h, k, H, K$  vary as well as the origin  $L'$ . The motion will therefore be represented by a variable elliptic superposed on a variable hyperbolic motion. If the former predominates the particle may remain near  $L$  for some considerable time; if the latter, it will rapidly depart from  $L$ . Moreover, it may happen that the disturbing force is such that  $h^2 - k^2$  passes through the value zero and changes sign. The orbit will then cross the asymptote and a particle which was approaching  $L'$  will begin to recede from it along the other branch of the hyperbola.

If therefore the initial value of  $h^2 \sim k^2$  is small, a small disturbing force may be sufficient to completely change the form of the orbit, even to transforming a direct into a retrograde orbit through the limiting cusped form which separates the direct from the retrograde members of a family.

XV. *On the Physical Interpretation of the Michelson-Morley Experiment.* By J. ROSE-INNES, M.A., B.Sc.†

THE theoretical aspects of Michelson and Morley's well-known experiment have given rise to considerable discussion. The explanation put forward by FitzGerald was eagerly acclaimed and is still widely accepted in substance: viz., that an elongation of the apparatus across the line of motion occurred, together with a contraction along the line of motion, of just sufficient magnitude to neutralize the difference in the times of passage of a light-wave due to a drift of the apparatus with respect to the æther. (See Lodge's Presidential Address to the British Association, 1913.) There is, however, no independent experimental evidence for this change of dimensions, Lord Rayleigh's attempt to detect it by means of a possible

\* "On certain discontinuities connected with Periodic Orbits," S. S. Hough. *Acta Mathematica*, vol. xxiv. 1901, pp. 257 to 288.

† Communicated by the Author.

double-refraction effect, as well as Trouton & Rankine's attempt by means of a change in electrical resistance, having both failed. (See Lord Rayleigh, *Phil. Mag.* 6th series, vol. iv. 1902; Rankine, *Science Progress*, July 1908.)

We may add to the failure of these tests the difficulty of believing that all solid substances, whatever their elasticity, should experience the same contraction when travelling with the same velocity.

The failure to confirm the FitzGerald contraction has led to the propounding of the theory of Relativity, in which, with a good deal of metaphysical subtlety, all our notions of time and space are revised. It seems to have been overlooked that a third solution is possible, viz., that, even though there be no dragging effect, such as Lodge searched for, a change in the constants of the æther may perhaps take place, owing to the motion of a large mass in the neighbourhood. Thus at the surface of the earth, the æther may be supposed to alter slightly in its properties, owing to the orbital motion. We may imagine that the velocity of an æthereal disturbance parallel to the motion of the earth is unaltered, but that at right angles to the orbital motion the velocity of a disturbance is

$$V - \frac{u^2}{2V},$$

where  $V$  is the velocity of light in free æther, and  $u$  is the velocity of the earth in its orbit. Any other simple function of  $V$  and  $u$  agreeing with the above as far as squares of small quantities would, of course, answer the purpose equally well in the present state of our experimental knowledge.

The correction-term suggested above is applicable to measurements at the surface of the earth; at considerable distances from the earth the effect of its motion ought clearly to be taken as smaller. Thus it is absurd to suppose that our optical determinations are sensibly affected by the orbital motion of Jupiter or Saturn. We may make allowance for the falling-off in the effect by supposing that the correction-term is more nearly represented by an expression of the form

$$\frac{u^2}{2V}(1 - e^{-G}),$$

where  $G$  is a function of the mass and the distance, akin to gravitation, in so far as it is large in the neighbourhood of

massive bodies and grows small as the masses grow smaller or the distances increase.

There is at present no method by which we can test the accuracy of the above formula. The Michelson and Morley experiment will naturally not serve as a test, since the correction-term has been actually chosen so as to cope with their results. The delicacy of our optical instruments in other experiments is insufficient to detect a term such as has been suggested above. Thus, theoretically, there will be an alteration in the accepted law of aberration for different directions, and there will also be a slight deviation from Snell's law of sines. But the former of these changes will involve less than one-millionth of a second of arc in our telescopic observations; while the latter would amount to less than one-thousandth of a second of arc in our measurements on the spectroscope. Both these quantities are at present utterly beyond our powers of observation.

The above formula is not opposed to the axiom of Relativity that the velocity of light in free æther is a constant. For we must mean by "free æther" any portion of æther freed from the influence of ordinary matter. Now by the above formula, when the moving matter has been taken to a sufficient distance so that its influence may be disregarded, the velocity of light becomes equal to a constant  $V$ . And all theories of light are bound to take note of the Fizeau effect, where it is definitely proved by experiment that the motion of matter may influence the velocity of light. A distinction is sometimes made between the case of a ray passing *through* moving matter, and one passing *near* moving matter. The distinction, however, if pressed too rigorously, would appear to disregard the principle of Huyghens and the atomic structure of matter. When a ray of light passes from the atom A to the atom B we are not concerned in Physical Optics, merely with what happens in the cylinder through A and B; strictly speaking the whole of the æther must be taken into account, though, of course, the predominant part in the propagation of the ray is taken by the æther within the cylinder. The flowing water in the Fizeau experiment consists of separate moving molecules, each of which may have its effect, and comparatively few of which lie directly between A and B.

The really important distinction between the influence of motion in the two cases is that in the Fizeau experiment we can give, owing to the work of Lorentz, a reasonable description of the machinery whereby the influence is

exerted, whereas in employing the above formula we have up to the present only suggested an empirical correction to accepted equations.

There is an imaginary experiment worth noting which would give different results according as we adopted the present theory or the theory of Relativity, and which might therefore serve as an *experimentum crucis*, could the experimental difficulties be removed. If we were to detach Michelson and Morley, together with their apparatus, from the earth and send them travelling along at the rate of 19 miles a second in the free æther, the absence of the earth would make no difference according to the theory of Relativity, but would cause a displacement of the fringes according to the present theory (provided that the mass of the experimenters and apparatus is not by itself sufficiently great to introduce a considerable effect of the kind here suggested). There are, however, very grave difficulties to the actual carrying out of this experiment, and it will certainly be some time before they are successfully overcome.

XVI. *The Hintereis Glacier*. By R. M. DEELEY,  
M.Inst.C.E., F.G.S., and P. H. PARR\*.

IN a previous communication to this Journal† we have shown that the ellipse is a very unsuitable form of curve to use for the purpose of studying the flow of such a glacier as the *Hintereis*, for it makes the edges of the ice-stream vertical instead of inclined. Some sections of glaciated valleys were plotted, and it was found that they approximate more closely to parabolas than to ellipses. The conditions of flow down parabolic channels have, however, not yet been ascertained. An attempt was, consequently, made to discover a form of channel which, while approximating to a typically glaciated valley, at the same time was one which could be used for ascertaining the conditions of flow in the *Hintereis Glacier*.

We have already discussed the curve which was found to be suitable and called it *Parr's curve* for convenience.

Since writing our paper on "The Viscosity of Glacier Ice," we have still further considered the question, especially as regards the cause of glacier slip and its probable amount; the conditions of shear stress and temperature within the glacier; crevassing and viscosity.

\* Communicated by the Authors.

† Phil. Mag. July 1913, p. 85.



It is clear that the slip of a glacier is due to the force of the downward component of gravity of the ice, acting all over the glacier-bed, and it is important to ascertain how this force is distributed across the section. The rate of shear in close proximity to the glacier-bed is proportional to this force.

Fig. 1 shows an ellipse with the surface-velocity curve above, and also the lines of equal velocity within the ice. Fig. 2 is the same ellipse with the lines of equal shear force.

Fig. 3 shows a form of Parr's curve, similar to the Hintereis Glacier profile at Section V., with the surface-velocity curves and the lines of equal velocity within the ice. Fig. 4 shows the lines of equal shear force within the glacier, across the glacier bed and upper surface, all expressed in kg. per cm.<sup>2</sup> (See Appendix.)

In these diagrams the viscous substance is regarded as adhering to the walls of the channel.

These curves show how very greatly the conditions of stress and rate of shear differ in a channel of the form of Parr's curve as compared with those in an elliptical channel.

*Slip of Glacier Ice.*—In our paper previously communicated to this Journal we write: "Very little is known concerning the coefficient of friction of glaciers upon their beds. Indeed, it is not clear why a glacier slips at all upon its bed when we consider how slight the slope generally is." Under the pressure to which the bottom ice is subjected it must penetrate into every crevice and irregularity of the rock below, and the interlocking of ice and rock might be considered as tending to prevent any slip at all.

The surface motion of glaciers has been found to be the sum of two movements, one a bodily slip of the whole mass of ice on its bed, and the other a result of the differential motion of the ice of the glacier. The differential motion which results in shear without fracture, and gives to a glacier its peculiar structure, has been the subject of much discussion and investigation. With regard to the nature of the slip little is known. The grooving, scratching, and polishing effected by glaciers might, at first sight, be regarded as due to a form of slip similar to that which occurs between a surface of lead into which emery has been pressed and the hard surface which it grinds. A closer examination of the phenomena shows that this resemblance is only partially true, for the cutting material is not held firmly in the ice, as is the case with emery and lead, and the ice, unlike the lead, penetrates into all the small irregularities of the rock surface upon which it rests.

In the case of a glacier the rate of shear at the slip surface between the rock and ice is generally slow and steady, and

Fig. 1.

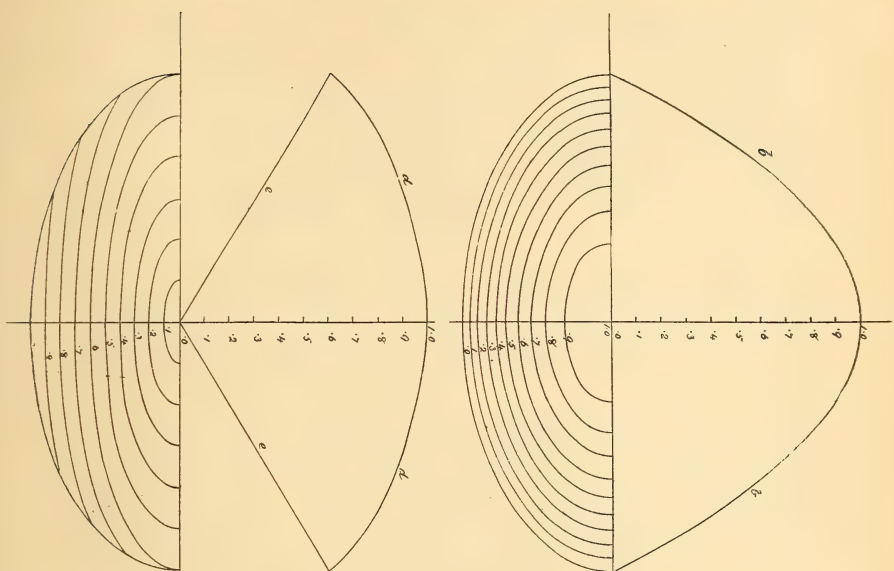
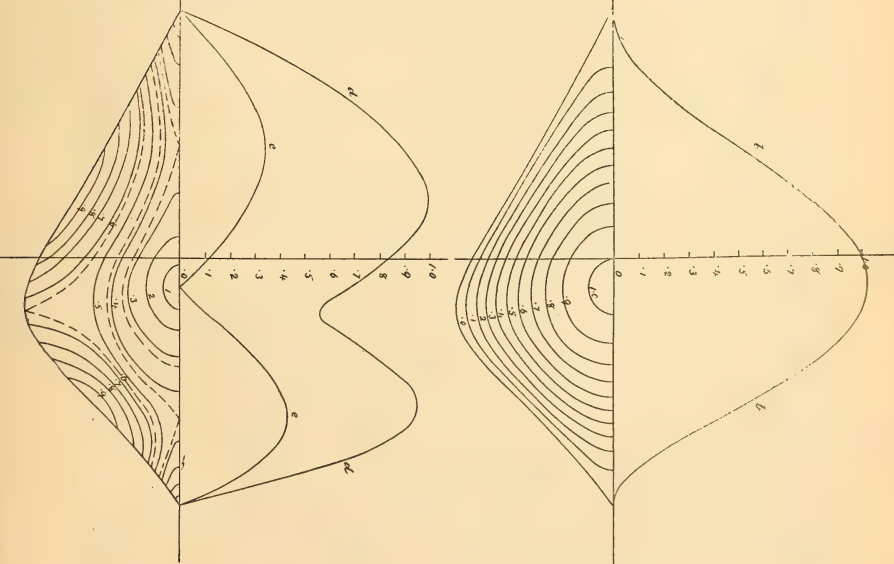


Fig. 2.



the velocity would appear, as we hope to show, to be approximately proportional to the downward force of gravity; but in the case of a grinding tool, such as that of the lead-emery surface, when slip occurs the motion is rapid and the coefficient of friction is regarded as being due to the interlocking of the asperities of the two surfaces, and the movement results in abrasion. Also, in the case of polishing or grinding, unless the stress be very considerable, the polishing medium does not slip at all.

We shall give grounds for holding that the motion or slip of *clean* ice upon a hard, but slightly rough surface, may take place without abrasion of either the rock or ice. According to this theory what is known as slip differs in the case of a glacier from our conception of the ordinary meaning of the word.

It is well known that the freezing-point of ice varies with the pressure. An old experiment which has lately been repeated by Tarr and Rich\* illustrates this property of ice. A loaded wire rests upon a block of ice. Owing to the pressure exerted upon the ice immediately below the wire, the ice is there melted, the water moves up the sides of the wire, and the pressure being relieved, freezes again above. There is thus set up a continuous flow of water from the underside of the wire to the upper side, and the wire cuts its way through the ice without destroying the continuity of the mass. In one of Tarr and Rich's experiments a block of ice 2·57 cm. thick was cut through in four minutes, the load being 70·32 kg. per cm.<sup>2</sup>, and the temperature  $-0\cdot055$  C.

When metallic wire is used the heat is rapidly conducted from the upper to the lower surface of the wire, and the sinking of the wire through the ice is rapid. We shall show, however, that when a slowly conducting material, such as glass, is used the action takes place much more slowly.

A smooth rock surface upon which a glacier rests may be regarded as being covered by numerous small projections which rise into the ice above. Against the up-stream sides of these projections the pressure of the ice is greatest, whilst on the down-stream sides it is least. On the up-stream sides melting, therefore, takes place, the water produced passing round the projections and freezing again on their lower sides. In this way the mass of ice is allowed to move slowly forwards over the somewhat rough surface.

If we consider the projections on the glacier bed to be pyramidal, with base angle  $\theta$ , then the area of the base is  $(2s)^2$ , the area of the vertical cross-section through the apex

\* *Zeit. für Gletscherkunde*, Band vi. Heft 4, p. 229.

will be  $s^2 \tan \theta$ , and the ratio of the former to the latter is  $4 : \tan \theta$ , depending upon the angle  $\theta$  only; so that the total resisting area is independent of the size of the projections.

According to this hypothesis the resistance of a rock surface to the slip of a mass of ice resting upon it will be proportional to the sum of the cross-sections of the projections on the surface, provided that the pressure holding the surfaces together is sufficiently great to prevent the ice from rising bodily up their inclined surfaces.

If we regard the rate of slip as proportional to the force parallel to the surface, and as being independent of the size of the projections, it is possible to calculate the angle of the sides of the conical protuberances which would allow a glacier to slip at known speeds.

Tarr and Rich found that the velocity with which the wire cut through the ice was 0.0107 cm. per sec. under a load of 70.32 kg. per cm.<sup>2</sup>. These experiments were made with metallic wires. Experiments have, therefore, been made with glass, which has a coefficient of conduction somewhat similar to rock.

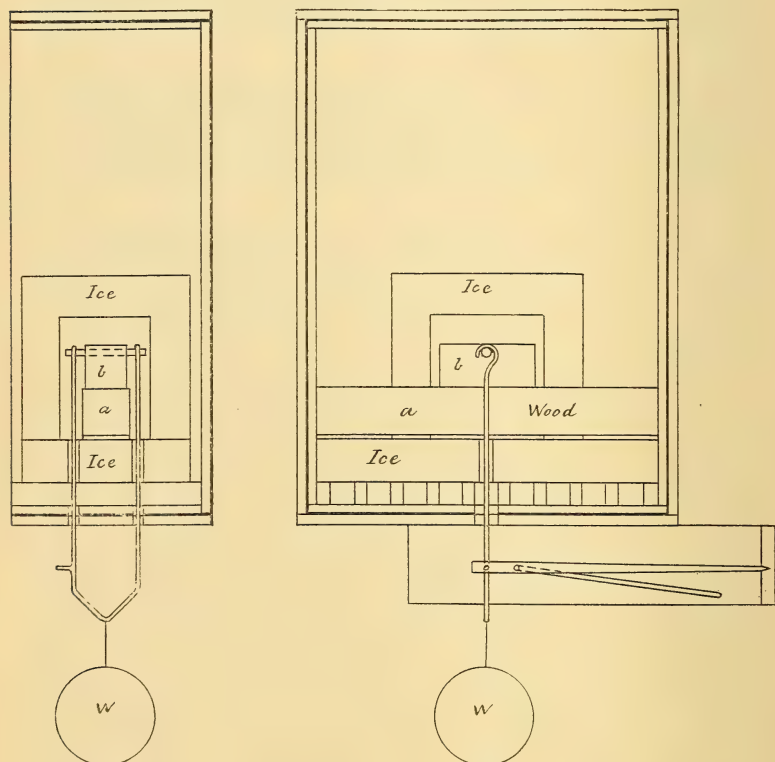
Fig. 5 shows the apparatus employed for the experiments. *a* is a bar of wood extending from side to side of a well insulated box. Below this bar, and resting upon laths, was placed a slab of ice about 1.5 in. thick. Upon the bar *a* was placed the piece of ice *b* to be experimented upon, and across it was fixed the glass rod which had a diam. of 0.7 cm. From the glass rod hung a sling of stout wire coated with sealing-wax, the wires passing through holes melted in the ice and then through the bottom of the insulated box. Covering the bar *b* was a hollow cover of ice, enclosing the ice bar *b* and the wooden supporting bar *a*, and resting upon the ice slab below. The box was fastened to a wall at a convenient height, a large piece of ice placed on the top, and the whole covered with flannel. To the sling carrying the weight was secured a lever multiplying 8.3 times. The readings of this lever registered the result of the melting of the lower side of the ice bar as well as the fall of the glass rod, but the error introduced by melting in contact with the wood could not have amounted to more than a very small percentage of the total.

After being fixed the apparatus was allowed to stand for about three hours with the load on the glass, after which readings were taken. When, after the experiments, the box was opened only a very small amount of melting was found to have taken place in the ice cavity surrounding the ice bar



*b*, and the glass rod was found to have embedded itself in the ice; most of the water produced by the pressure beneath the glass had found its way to the upper side and the pressure being relieved it had frozen there. Before putting the glass bar in position a groove was melted along the top of the ice bar and in this groove the glass bar was placed.

Fig. 5.



Tarr and Rich found that when the temperature was a few degrees below the freezing-point the rate of cutting was very slow, and when the pressure was also small the rate of cutting became almost unmeasurable. It is, therefore, very important that the experiments should be made at or very slightly above the melting-point. In the experiments, the results of which we give, the atmospheric temperature was about  $15^{\circ}$  C. and no freezing mixture was used.

Taking the case of the Hintereis Glacier we have, at Blümcke and Hess's section V., estimated the slip to be

21.5 metres per annum, or 0.000068 cm. per sec., and the slope to be 9 in 100, which corresponds to an average shear force across the central two-thirds of the glacier bed of 0.84 kg. per cm.<sup>2</sup>. Our experiments with the glass bar give a cutting velocity of 3.0 mm. in 24 hours, or 0.00000347 cm. per sec. under a pressure of 2.06 kg. per cm.<sup>2</sup>; so that, if the resisting area of the asperities on the glacier bed amounted to 1 cm.<sup>2</sup> per 1 cm.<sup>2</sup> of bed, the slip would be, using these figures as a basis,

$$\frac{0.84 \times 0.00000347}{2.06} = 0.00000141 \text{ cm. sec.}$$

The actual rate of movement being 0.000068 cm. per sec., the asperities must, on this basis, amount to  $\frac{141}{6800} = 0.0207$  cm.<sup>2</sup> per cm.<sup>2</sup> of bed, and their angle must be

$$\tan^{-1}(4 \times 0.0207 = \tan^{-1} 0.0828 = 4^{\circ} 44'.$$

Small asperities having angles of  $4^{\circ} 44'$  would produce an average roughness which cannot be considered as much rougher than a glacier-bed. With the temperature at the freezing-point the angle would be somewhat less. The theory, therefore, gives results which are of the proper order of magnitude.

The very small irregularities of the glacier-bed are not, of course, the only hindrances to motion. The glacier has to change its form to accommodate itself to the bends and larger irregularities of its channel. Here the resistance to flow is a purely viscous one. Boulders, grit, and fine material are embedded in the lower surface of the ice, and this material is not held firmly in the glacier surface. The viscous yield of the ice, as well as the thawing and freezing due to varying pressure, allows the boulders &c. to move in the ice surface as they score the rock below. When the ice enters crevices and hollows it must be actually sheared.

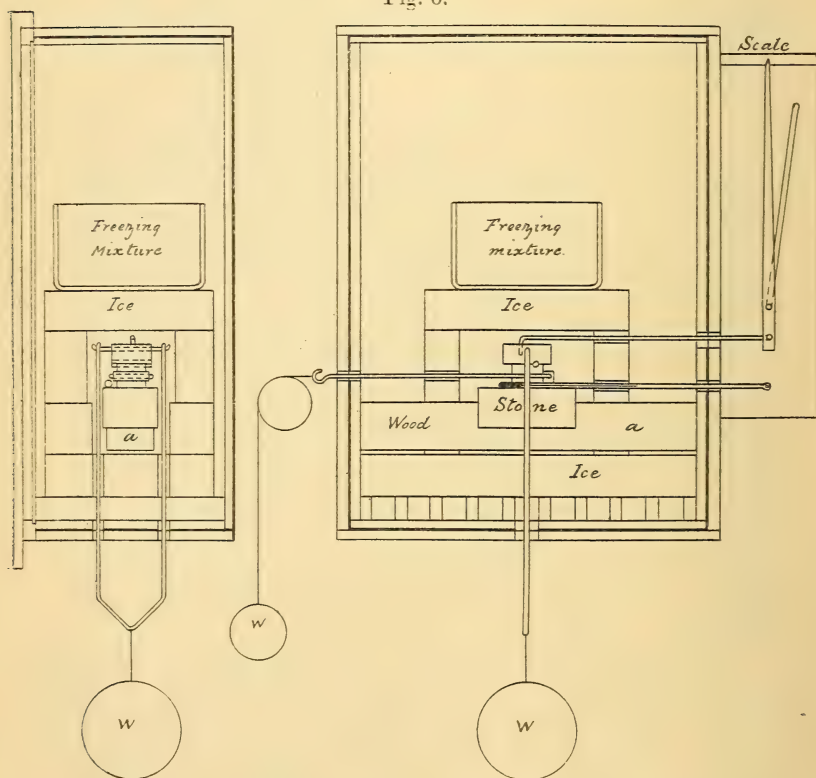
We have called attention to the fact that the glacier is held down by its weight, and the asperities are compelled to cut their way through the ice surface. Now if the angles of the asperities were all  $4^{\circ} 44'$ , and the slope of the glacier were much greater than this angle, there would be a tendency for the glacier to slip forward, especially if the surfaces of the asperities were smooth. In the case of the Hintereis Glacier the slope at section V. is  $5^{\circ} 9'$ , or a little steeper than the figure obtained for the asperities.

If the theory propounded be sound, then the slip is proportional to the shear stress on the glacier-bed.

The theory also makes the velocity of the slip proportional to the thickness of the glacier, whereas the surface speed, due to the differential movement of the ice resulting from its viscosity, is proportional to the square of the thickness of the glacier, and the slip and viscous flow are about equal when the shear stress on the glacier bottom is about 1 kg. per cm.<sup>2</sup>.

*Measurement of slip.*—After making the experiments on the downward movement, under load, of a glass bar into ice, the apparatus was altered so as to enable the slip of a piece of ice on a stone surface to be measured.

Fig. 6.



The stone was brought to a smooth level surface by grinding. It was then scratched diagonally with the edge of a second-cut file. The stone upon which the ice rested was fixed in the wooden bar *a* (fig. 6). Three V-shaped grooves were cut with a file longitudinally on the stone, to

prevent the ice from sliding sideways before it had become embedded in the stone, and upon the ice rested a piece of wood upon which a weight of 11·3 kg. was slung. To prevent this piece of wood from sliding on the ice, a glass rod was half embedded in the wood and half in the ice. From this piece of wood ran a rod connecting it with the recording lever. Another sling, secured to a piece of wood, served to carry a load whereby pressure was brought to bear upon the ice sample for the purpose of causing it to "slip" over the stone below in a direction parallel with the grooves in the stone.

The whole was surrounded with blocks of ice as before, and a thermometer-bulb lay in the ice-cavity containing the ice sample to be tested.

To get the temperature below the freezing-point, a dish of ice and salt was placed upon the ice surrounding the bar, and two other small cans with salt and ice were placed at the sides.

In about four hours' time the temperature had fallen to  $-0^{\circ}\cdot3$  C. In another hour and twenty minutes the temperature was  $-0^{\circ}\cdot8$  C. The load used to cause the ice to slide on the rock was in position, but no movement took place at these temperatures and the ice was firmly frozen to the rock. During the next three hours the ice did not move, and the temperature slowly fell to  $0^{\circ}\cdot0$  C.

The insulation of the box was then improved by covering it up with flannel, the load tending to cause the ice to slip removed, and the whole allowed to rest for nine hours. At the end of this interval the temperature was still  $0^{\circ}\cdot0$  C., and the recording finger showed that no appreciable slip had occurred.

The load to produce slip was then put on, and the readings shown on diagram fig. 7 obtained. It will be noticed that some time after each slight rise of temperature the velocity of slip very slightly increased, and that when the temperature fell the velocity of slip decreased.

*Data :—*

Hours in a year = 8760.

Mean slip during seven hours =  $0\cdot017$  cm. per hour.

Shear force during test =  $0\cdot907$  kg.

Area of ice sample =  $13\cdot4$  cm.<sup>2</sup>.

Shear force at centre of glacier =  $0\cdot822$  kg. per cm.<sup>2</sup>.

This is the mean over about three-fourths of the central portion of the glacier.

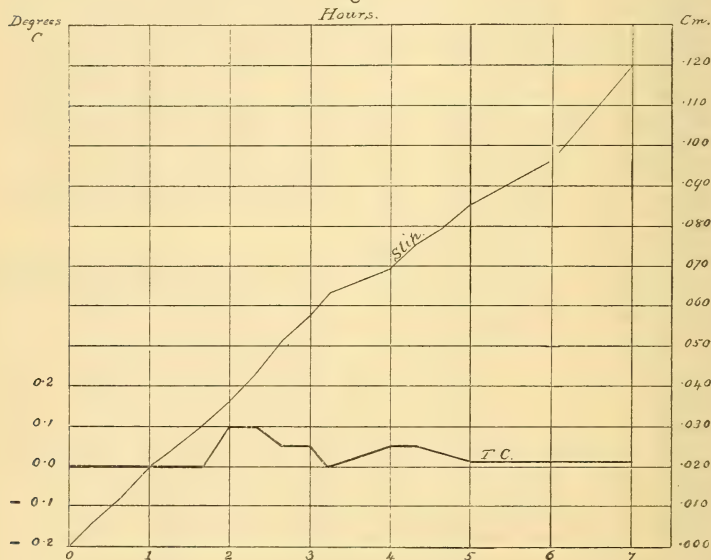
$$\text{Slip} = \frac{8760 \times 0\cdot017 \times 13\cdot4 \times 0\cdot822}{0\cdot907}$$

$$= 18\cdot08 \text{ metres per annum.}$$



In our previous paper we took the slip of the Hintereis Glacier to be 21·46 metres per annum. That the two figures should be so nearly alike is due to the accident of the roughness of the slab.

Fig. 7.



The experimental results tend to show that the theoretical movement, or slip, is of the right order of magnitude, and that, therefore, the slip of a glacier is due very probably to the melting and refreezing which takes place where each little irregularity of the glacier-bed projects into the ice.

*The Conditions of Flow of the Hintereis Glacier.*—In our previous communication we assumed that the rate of slip was proportional to the load on the glacier as well as the downward force of gravity, and also that the channel was an ellipse. A consideration of the conditions of shear stress in a glacier moving down a channel of the form of Parr's curve, and with a velocity proportional to the shear force on the bed, leads to some results which agree well with the actual surface-velocity of the Hintereis Glacier, and tend to support the theory of slip we have described.

We will in the first instance assume that the actual surface-velocities of the glacier are the sum of the slip and viscous velocities, and that the rate of slip at various points is not modified by the high viscosity of the ice tending to make the slip more regular across the section.

In our previous paper\* we adopted the statement of Finsterwalder that that led us to regard the summer velocity as 15 per cent. in excess of the winter velocity. This seemed likely to be correct, in view of the measurements of Forbes and Tyndall. Blümcke and Finsterwalder †, however, have since given the results of a large number of measurements made at many points along the tongue of the Hintereis Glacier. The results of these measurements constrain them to say that some outstanding irregularities and exceptions in the tables urged them at the commencement, and in the progress of the investigations to adopt views which they have retracted in favour of others more recently brought forward, and which rest on a consideration of the whole of the measurements.

Their full results clearly show that it is only along the end third of the glacier tongue that the summer velocity is greater than the winter velocity. In the upper two-thirds of the glacier tongue the winter velocity is the greater. The authors say:—"The reason for this surprising phenomena we find in the following considerations. The driving force of glacier movement is manifestly gravity, and the pressure of the névé layers produced through it. One resistance to glacier movement proceeds from the interior friction of the ice-mass and from friction on the glacier-bed. The velocity-condition of the glacier originates from the cooperation of driving force and resistance; the winter acceleration of movement in the upper parts is in the first place attributable to the increased névé pressure in the winter; while the summer acceleration of movement in the lower parts must be traced to lessened friction-resistance, in consequence of penetration of the ice and glacier-bed by melting water."

Blümcke and Finsterwalder found approximately that the summer speed was greater than the mean velocity in the lower parts of the glacier by about the following percentages:—At 350 metres from the end, 27·8 per cent.; at 600 metres, 15·0 per cent.; and at 774 metres, 10·3 per cent. On the contrary, at 1750 metres the mean velocity was 11·2 per cent. and at 2700 metres 18·3 per cent. greater than the summer velocity, and continued to be greater well into the névé region. At section V., therefore, instead of the winter velocity being less than the summer velocity, it is greater.

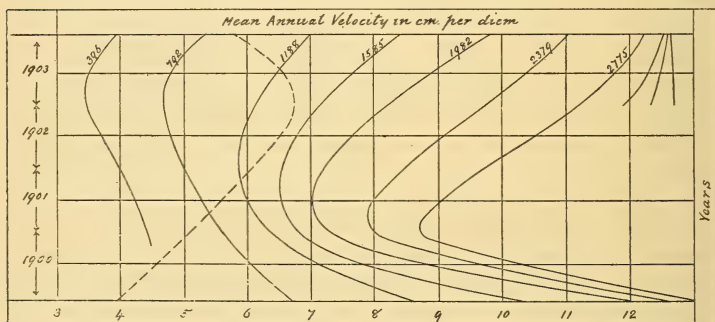
\* Phil. Mag. vol. xxvi. pp. 85-111 (1913).

† *Sitzungsberichte der math.-phys. Klasse der K.D. Akademie der Wissenschaften zu München*, Band xxxv. (1905). München, 1906. Pp. 109-131.

Owing to these considerations it would appear that at section V. the interior ice of the Hintereis Glacier is not affected appreciably by the summer heat, even near the surface, and that we must regard the ice at section V. as being about equally "dry" throughout. However, it may be that there is more interstitial water in the ice near the bottom than at the surface, owing to the greater shear that takes place there. On the other hand, the temperature of the snow which forms the glacier ice may be so low that the interior ice of the glacier is never raised to the melting-point by the internal friction.

Blümcke and Finsterwalder measured the variations of velocity on the glacier tongue during a period of several years. Their results, as exhibited by their observations made at points some distance from the glacier sides, have been plotted, and the diagram (fig. 8) constructed to show the

Fig. 8.



changes of velocity that occurred in the glacier tongue. At a distance of 2775 metres from the end of the glacier the velocity reached a minimum early in 1901. This minimum shows itself at a point 396 metres from the end of the glacier early in 1903. The dotted line shows, approximately, the rate of retreat of the glacier snout, a decreasing velocity of the ice being accompanied by an increased rate of retreat, and *vice versa*.

It is now recognized that variations of the velocity of a glacier tongue are generally due to a general lowering of the snow-line and not to increased precipitation. Of course, increased general precipitation would lower the snow-line, but glacier advances are not generally due to this cause. In some cases where the precipitation had been temporarily greater than usual, it would appear that the damp winds

which occasioned it were warmer and the snow-line was raised, the one effect neutralizing the other. When, however, the snow-line is lowered, the névé or alimentation area is increased and the tongue area or main ablation area is decreased—at the snow-line these two areas overlap. But as the total snow-fall in the alimentation area must be melted in the ablation area, the glacier tongue ultimately advances if the lowering of the snow-line persists for any length of time. In other words, although the precipitation has not increased, the area over which snow falls rather than rain has increased, and the glacier tongue advances until the ablation area is large enough to get rid of the increased quantity of snow flowing down from the névé. However, the effect of the greater quantity of snow falling on the increased névé area does not at once affect the glacier snout. In fig. 8, at a distance of 2775 metres from the end of the glacier, from 1901 forwards, the velocity of the ice was increasing, but during the same time, the velocity on the point of the ice, 396 metres from the end, was decreasing, and continued to do so until the commencement of 1903. A period of cold during which the snow-line is lowered does not on this account affect the ends of all glaciers at the same time. The advance or decreased rate of retreat is more delayed the longer the glacier is. Indeed, in the case of a long glacier it *may* altogether exhaust itself before reaching the end.

The sensitiveness of the ice movement to changes of thickness and changes of slope render it probable that no great error is generally likely to be introduced into calculations of viscosity by taking the conditions of slope, &c., at any particular moment. We shall, therefore, consider that the mean annual velocity we have used, instead of being decreased by 10·2 per cent. to get the winter velocity, should be decreased by 11·2 per cent. so as to get the summer velocity to compare with the summer slope measurements. We did not previously recognize that the accumulated winter snow made such a difference in the winter velocity of the glacier tongue. It will be seen that the alterations in the figures thus introduced are too small to render any correction of the figure for viscosity necessary, since the actual summer velocity is nearly equal to our theoretical winter velocity, and the ice is probably dry and little affected by heat, even in the summer.

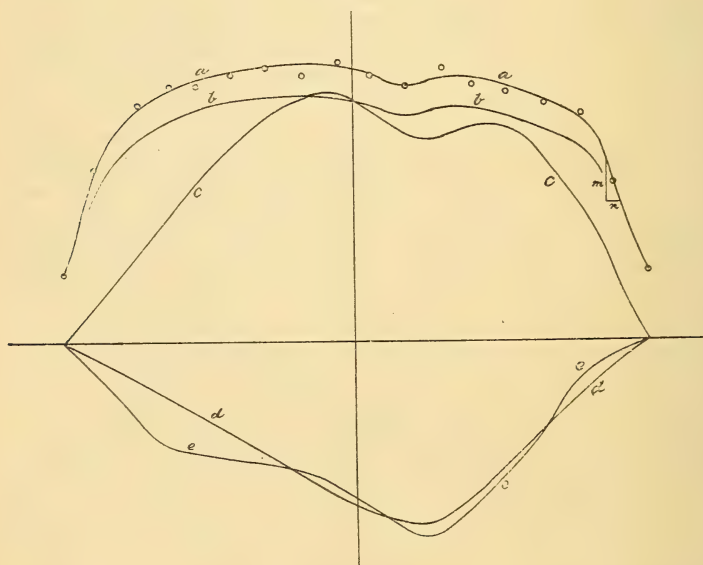
In some cases where the thickness of the ice has rapidly increased in the lower portions of the névé, the ice comes down the glacier in distinct waves or *Schwellungswellen*, which travel three or four times as fast as the ice and become



more and more pronounced as they advance. A thickening of the upper portion also gives rise to an increased velocity by thrust, and such pulses are known as *Druckwellen*, which travel down the glacier from 20 to 150 times as fast as the ice itself. Blümcke and Finsterwalder, in the case of the velocity curves of the Hintereis Glacier, shown in fig. 8, state that they did not notice waves which could be regarded as *Schwellungswellen*, phenomena which might render any measurements of velocity and slope near them somewhat misleading if used for the calculation of viscosity.

In fig. 9, *a* is the mean annual velocity curve across the

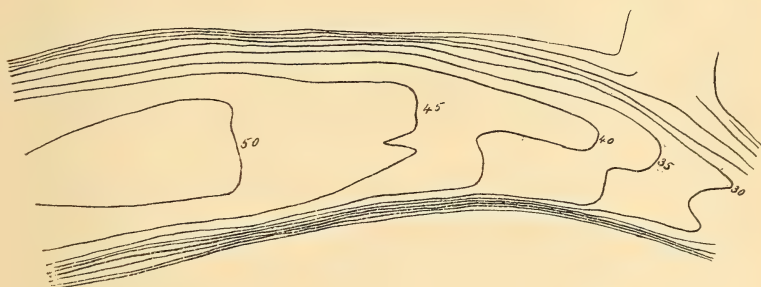
Fig. 9.



glacier, *b* the summer velocity, and *c* the calculated velocity curve on the assumption that the central surface-velocity due to differential flow is 21 metres per annum and the slip 21 metres per annum. The curve *c* was obtained by combining the curves *b* (fig. 3) and *d* (fig. 4). It is interesting to note that both the theoretical and the actual curves show a smaller velocity over the deep side of the glacier than they do over the shallow side. The curve *d* (fig. 9) is Parr's curve and *e* the actual section of the Hintereis Glacier. In our former paper the velocity curve was plotted in accordance with the equal velocity curves drawn by Blümcke and Hess. In fig. 9 the small circles represent the actual velocities

found at numerous points on the surface at section V. It will be seen that not only is there a lower mean velocity on the deepest side, but that near the centre there is a distinct lowering of the actual velocity curve between the deepest portion of the glacier and its centre. That this is not an accidental local feature is shown by fig. 10, which shows a

Fig. 10.



Lines of equal velocity on the Hintereis Glacier.  
Velocities in metres per annum.

line of low velocity near the centre extending throughout the glacier tongue. In drawing their equal velocity curves, Blümcke and Hess did not give any weight to certain apparently irregular velocity determinations near the middle. In figs. 9 and 10 we have drawn the equal velocity curves as strictly as possible in accordance with the velocities observed by Blümcke and Hess.

The reason why the summer velocity curve *b* (fig. 9) does not agree more nearly with the theoretical curve *c*, is no doubt due to the fact that the ice at the shallow sides is dragged along by the rapidly moving central portion, and also because the depth of the ice at the shallow side is greater than in the case of Parr's curve. The great viscosity of the ice has also resulted in the velocities being more even over the central portion of the glacier. We have previously suggested that the reason why the greatest velocity is over the shallow side is probably partly due to the curve of the valley. It now seems that it is mainly due to the varying amount of slip across the glacier-bed.

The fair agreement in all essential particulars between the actual and theoretical curves strongly supports the theory that "slip" is proportional to the shear force on the bottom and is independent of the load. It also favours the inference that slip is responsible for a large proportion of the total surface-velocity.

Many other glaciers give a different form of surface-velocity curve from that of the Hintereis. This no doubt results from different forms of the valley cross-sections.

*Temperature of Ice.*—Glacier ice, resulting as it does from the consolidation of snow in the n v  regions, may, for several seasons, contain interstitial water. The presence of such water would have a considerable effect upon the fluidity of the mass. The question is one, therefore, of considerable interest from the point of view of the theory of glacier motion.

During the greater part of the day in summer in the region of the n v , in the case of glaciers in low latitudes, the heat of the sun melts and softens the snow very considerably. It is to this moistened snow-surface that the brilliant reflexion is due which adds so considerably to the beauty of a snow scene in high alpine regions. The water thus produced sinks into the snow, and, except in high latitudes and at great altitudes, it may not all be frozen again by the cold of night. On this account glacier ice may contain water-cavities. It does not follow that such water would exist in a capillary condition. Rather should we expect to find it as globular masses in otherwise solid ice.

During the winter the temperature of the n v  regions is much below the freezing-point, and the snow which falls is at a very low temperature. Although snow is a bad conductor—and on this account it has been argued by Hess that the snow-covering would prevent the cold of winter from penetrating the ice—it might also be argued, as Hess did at a later date, that as the snow falls at a low temperature, heat could not penetrate it, and it would remain cold. Unfortunately we know very little concerning the temperature of the ice in the n v  regions. A tunnel driven into the ice-cap on Mont Blanc showed that the temperature at a depth of 13 metres was  $-16^{\circ}5$  C. Indeed, a good deal of the ice coming down from the higher regions must be considerably below the freezing-point, and tend to prevent the accumulation of water in the ice due to the heat of the summer.

Another cause which tends to produce water in glacier ice is the pressure resulting from the accumulation of snow.

Every part of a glacier was once at the surface in the névé regions. As layer upon layer of snow collects, the weight of the snow above results in the lowering of the freezing-point, and, if the temperature of the ice be at the freezing-point, results in the formation of some interstitial water. When the region of ablation is reached, the thickness of the glacier diminishes, and some of the water again returns to ice.

The variations of temperature with depth have been determined in some parts of the tongue of the Hintereis Glacier with considerable accuracy by Blümcke and Hess. They used thermometers which showed temperature variations amounting to thousandths of a degree centigrade. The thermometers were immersed in holes bored into the glacier. Their bulbs were embedded in paraffin and did not undergo any change of temperature whilst being drawn up from the positions in which they had been allowed to rest for a long time.

The following table gives the results obtained :—

Metres depth.	Temp. C.	Temp. fall per kg.
30	—0·0215	—0·000234
40	—0·0400	—0·000326
42	—0·0380	—0·000295
54	—0·046	—0·000278
66	—0·055	—0·000272
78	—0·062	—0·000259
82	—0·062	—0·000247
148	—0·137	—0·000302
		8·002213
		·000276 Average.

As the boreholes in which the temperatures were taken by Blümcke and Hess were full of water, the temperatures found should be those due to the pressure of the head of water, and if the temperature of the glacier were that due to the pressure of the column of ice above, then in the borehole some melting would take place and the temperature would fall to that required by the column of water. On the other hand, if the temperature of the glacier were below the temperature due to the head of water in the borehole, then the water in the borehole would slowly freeze. Blümcke and Hess state that no such freezing was noticed. But the temperatures obtained show a gradient per kg. of water-pressure even larger than the theoretical, as will be seen below :—

Experimental by Kelvin . . . . .	0°·000249 C. per kg.
Theoretical by James Thomson . . . . .	0°·000231 C. „
Experimental borehole by Blümcke } and Hess . . . . . }	0°·000276 C. „



Blümcke and Hess are of opinion that their results are extremely accurate, and that the low temperatures they found cannot be ascribed to experimental errors. It is clear, therefore, that either the theoretical and experimental results of Thomson and Kelvin are too small, or that the temperature of the glacier is slightly below the freezing-point to a depth of at least 148 metres.

This could only come about by the temperature of the snow falling on the névé being much below the freezing-point; so much below the freezing-point that the heat liberated by friction has not been able to melt any of it down to a depth of 148 metres.

*Internal Heat of friction.*—There is also a further reason to suppose that water may be formed in the interior of glaciers. During the descent of the ice from higher to lower regions viscous shear takes place and the internal friction generates heat. If this heat could not escape, some of the ice would thaw.

The heat liberated by friction in the ice is greatest near the bottom, where the rate of shear is greatest, and decreases rapidly towards the surface.

The heat liberated in a column of ice 1 metre square and 200 metres high (which is about the thickness of the Hintereis Glacier) in one year = weight  $\times$  fall  $\div$  mechanical equivalent of heat.

The weight of 1 m.<sup>2</sup> of ice 200 metres high

$$\begin{aligned} &= (100)^2 \times 20000 \text{ cm.}^3 \times 0.9 \times 981, \\ &= 1.765 \times 10^{11} \text{ dynes.} \end{aligned}$$

The average velocity of the ice for a surface speed of 21 metres per annum is 14 metres per annum. With a 9 per cent. grade this gives a vertical fall of 126 cm. per annum.

Work, therefore,

$$\begin{aligned} &= 1.765 \times 10^{11} \times 126, \\ &= 2.22 \times 10^{13} \text{ ergs,} \\ &= 534,900 \text{ gram calories.} \end{aligned}$$

*Flow of Heat in Glaciers.*—The only means by which water in a glacier can be frozen, other than by a low external temperature, is by the presence of a temperature gradient in the ice. Such a gradient would exist in a wet glacier, and it remains to be seen if this gradient is sufficient to get rid of the water produced by friction.

It was shown by J. Thomson from theoretical considerations that the freezing-point should be lowered 0°·000231 C. per kg. of pressure, and Kelvin obtained experimentally a

reduction in the freezing-point of  $0^{\circ}\cdot000249$  C. per kg. Taking the theoretical figure we should have in a glacier a gradient of about  $0^{\circ}\cdot1$  C. per 14,800 cm. Using a coefficient of conduction for ice of 0.0057 the flow of heat per annum per sq. metre

$$= \frac{0\cdot0057 \times 10000 \times 31536000 \times 0\cdot1}{14800}$$

$$= 12,000 \text{ gram calories.}$$

This is only about one forty-fifth part of the heat produced by friction, so it would seem that unless the ice coming from the higher slopes is much below the freezing-point, glacier ice, especially near the bottom, must contain some water.

*Crevasses.*—In addition to being a substance possessing a very high viscosity, ice is also brittle and elastic. The brittleness of ice is well shown by the numerous crevasses which score glacier surfaces.

The most simple form of crevasse is that which occurs at an ice fall; the crevasses then run across the glacier. But there are crevasses which run roughly at angles of  $45^{\circ}$  or  $60^{\circ}$  with the sides, and extend from the edge in an upward direction, while others run longitudinally or nearly so. The explanation generally adopted for the inclined crevasses is that put forward by Hopkins.

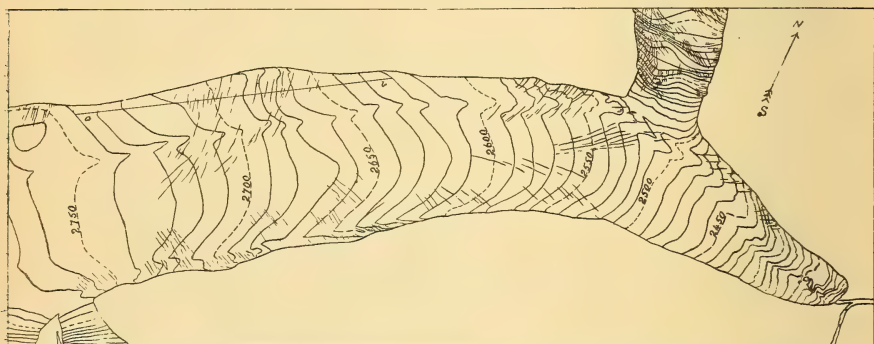
Hopkins pointed out that as a glacier moves more slowly near the sides than it does in the middle, surface distortion takes place as a result of shear, and that in such a case compression and tensile strains are set up which reach a maximum at  $45^{\circ}$  with the side. These tensile strains were assumed by him to be sufficiently great to cause rupture. Hitherto our knowledge of the distribution of the crevasses caused by glacier flow has not been sufficiently detailed to allow of a thorough examination of the sufficiency of this theory to explain the facts.

Blümcke and Hess, however, have supplied the details necessary for such an examination in the case of the Hintereis Glacier. Fig. 11 is a map of the glacier tongue showing the crevasses and the contour-lines. Owing to the surface shear being partly the result of slip, the actual velocity curve across the glacier is as shown by curve *a*, fig. 9. Here the maximum rate of shear is near the side, and the shear force is  $\eta \frac{m}{n}$ .

$$= 125 \times 10^{12} \frac{\cdot00001236}{1670} = 0\cdot94 \text{ kg. per cm.}^2$$

If it were not that the effects of slip assist viscous flow to produce surface stresses, there would be less strain near the

Fig. 11.



Crevasses and Contour-lines on the Hintereis Glacier.  
Heights in metres.

sides to produce crevasses than is actually the case. However, by taking the actual velocity curve *b*, fig. 3, as we have done in the above calculations, the locus of the actual greatest shear force is dealt with.

The calculation shows that although a strain is set up in the ice by shear, the tensile stress at an angle of  $45^\circ$ , which is equal to the shear stress, it is not sufficiently great to produce crevassing; for ice will not rupture under a load of less than 28.5 kgs. per  $\text{cm}^2$ , or about thirty times as much as the shear stress gives rise to.

The considerations which led Hopkins to promulgate his theory are as follows:—

Unit area of surface in moving down the glacier undergoes compression in one direction and tensile stress in another. If the longitudinal and the corresponding transverse shears be  $f$  per unit area, then the stresses on any section inclined upwards at an angle  $\theta$  with the side of the glacier evidently consist of

$$(a) \text{ a tension } p = 2f \cos \theta \sin \theta \\ = f \sin 2\theta,$$

$$(b) \text{ a shear } q = f(\cos^2 \theta - \sin^2 \theta) \\ = f \cos 2\theta.$$

Crevasses may be considered to be produced by tension, so we have to consider the variation of tensile stress with angle.

Since the tensile stress  $p = f \sin 2\theta$ , it is a maximum when  $\sin 2\theta = 1$  or  $\theta = 45^\circ$ .

It will be noticed that owing to the nature of the shear movement of the glacier the inward end of the crevasse moves more rapidly than the outward end, and so the crevasse, after forming, rotates away from the bank; therefore such crevasses, except at the moment of formation and before opening, would be inclined to the bank at a greater angle than  $45^\circ$ . But although these peculiarities follow from the theory, there is the fatal objection that the actual stresses produced by viscous flow are not nearly sufficient to rupture the ice; indeed the conditions of stress in a viscous substance flowing down a channel of uniform section and slope are opposed to the formation of crevasses.

That very many crevasses are the result of strains set up in the ice by irregularities of the glacier-bed has been very generally accepted, and it is very probable that all crevasses are due to this cause.

For the explanation of crevassing we must, therefore, look to irregularities in the glacier-bed, and if it can be shown that crevasses would be formed by changes of slope, whose direction would be up the glacier and whose angle would be about  $45^\circ$ , such an explanation would be more satisfactory.

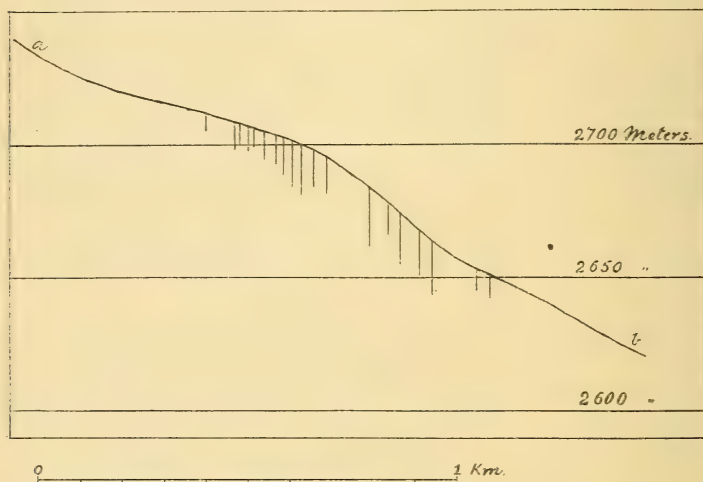
Referring to the map of the Hintereis Glacier, fig. 11, it will be seen that on the northerly side there are three groups of crevasses separated by clear spaces. The small group on the 2750 contour-line occurs where there is a change of slope. Between the 2750 contour and the 2710 the slope becomes less steep and there are no crevasses. From the 2710 to the 2650 contour the slope again steepens, the contours being crowded together, and the ice is much broken. These crevasses extend to the middle of the glacier, and their angle with the sides becomes less and less as the centre of the glacier is approached. We have seen that in the middle of the glacier there is very little shear and tensile stress, the speed curve being very flat, and yet there are crevasses. Here there is a marked increase in the slope of the middle of the glacier from the 2750 contour to the 2690. Fig. 12 shows a section along the line *a, b*, fig. 11. The vertical lines show the positions of the crevasses and their length, not their depth. From the 2650 to the 2590 contour there is a decreasing gradient and there are no crevasses. At the 2590 contour the slope again becomes steeper, and crevasses are numerous down to the 2550 contour.

On the southern side of the glacier the same features, but in a less marked form, are evident.



Between the 2610 and the 2520 contours, near the middle of the glacier, are some crevasses which are nearly parallel with the centre line of the glacier. Here, again, they are in positions where the ice shear is small and quite unable to produce appreciable viscous-flow stresses.

Fig. 12.



In all cases where the ice slope is becoming steeper crevasses are formed, but where the slope is becoming less steep they do not appear. However, the crevasses do not run straight across the glacier, but point upwards. There must, therefore, be some other stress set up when a change of slope takes place, which gives the upward direction to the crevasses.

One of the principal causes of the changes of slope which a glacier undergoes at the sides is due to the presence of shoulders of rock, separated by bays, which run down the mountain sides. Where the glacier is mounting such a shoulder it is also getting narrower, and two compression stresses are produced at about right angles to each other. When the glacier has mounted the shoulder, the increasing angle of slope brings into play a tensile stress tending to produce fractures normal with the valley sides. At the same time the sides of the glacier sink into the bay succeeding the shoulder, and a tensile stress is set up whose direction tends to produce longitudinal fractures. The actual crevasses are along the resultant line of maximum stress produced by these two forces. Although the differential

flow-stresses are small, they assist to produce crevasses running up the glacier and having the same angle of slope with the sides of the glacier as those produced by the shoulders and bays of the valley sides.

The tendency to produce longitudinal crevasses will be constant where the glacier is flowing down a valley the sides of which are getting less steep; for the sides will be sinking and cross tensile stresses will be set up. The central nearly longitudinal crevasses of the Hintereis Glacier appear to be due to this cause.

We thus appear to have stresses set up in a glacier flowing down valleys whose sides have been cut into by stream erosion, which will give rise to crevasses inclined upwards from the sides. Also, where a valley is getting wider and the sides less steep, longitudinal crevasses will be produced near the middle of the glacier. The strains produced by differential flow, called attention to by Hopkins, are much too small, of themselves, to produce crevasses, although they may assist the other forces to give the crevasses the upward trend.

*Viscosity of Glacier Ice.*—Our previously given equations, (21), (22), and (23), would have been better written as follows:—

$$\eta = \frac{P}{2v} \left( \frac{a^2 b^2}{a^2 + b^2} \right)^2 \quad \text{should be} \quad \eta = \frac{P b^2}{2v} \left( \frac{a^2}{a^2 + b^2} \right)^2,$$

for  $b$  belongs to the factor for infinite width and  $\left( \frac{a^2}{a^2 + b^2} \right)^2$  is the factor  $F_p$  for Parr's section, the factor  $F_e$  for the elliptic section being  $\frac{a^2}{a^2 + b^2}$ .

Equation (22) becomes

$$F_p \times \frac{F_a}{F_p} = 0.583 \times \frac{0.526}{0.580} = 0.523,$$

and (23) becomes

$$\begin{aligned} \eta &= \frac{79.46 \times 19900^2}{2 \times 0.0000654} \times 0.523 \\ &= 125 \times 10^{12} \text{ poises.} \end{aligned}$$

The alteration, it will be seen, does not alter the value obtained for the viscosity of glacier ice.

In equation (11)  $\frac{1}{\eta}$  should be  $\frac{1}{\eta}$ .

## APPENDIX.

*The distribution of shear force in a viscous fluid flowing along Parr's channel.*

As explained in our previous paper\*, the equation to Parr's curves is

$$0 = C - \alpha x^2 - \beta y^2 + \gamma x + \delta(x^3 - 3xy^2) \\ + \epsilon(x^4 - 6x^2y^2 + y^4) + \zeta(x^5 - 10x^3y^2 + 5xy^4),$$

where  $C = 1 - \frac{w}{K}$ ,  $w$  being the velocity parallel to the axis of  $z$ ,  $K$  the central surface velocity, the channel being given  $w=0$ , or  $C=1$ . Also, for a channel approximating to a natural valley, the equation must be of the form

$$(x+a^2)(x-a)^2(x+c) \text{ when } y=0.$$

The shear force at any point is equal to  $\mu \frac{\partial w}{\partial n}$ , where  $\mu$  is the coefficient of viscosity, and  $\partial n$  is an element of the normal to the curve  $w=\text{const.}$  passing through the point. Also

$$\frac{\partial w}{\partial n} = \frac{1}{\frac{\partial f}{\partial w}} \sqrt{\left(\frac{\partial f}{\partial x}\right)^2 + \left(\frac{\partial f}{\partial y}\right)^2}$$

where  $f$  represents Parr's function as above.

Differentiating,

$$\frac{\partial f}{\partial x} = 5\zeta x^4 + 4\epsilon x^3 - 3(10\zeta y^2 - \delta)x^2 \\ - 2(6\epsilon y^2 + \alpha)x + (5\zeta y^4 - 3\delta y^2 + \gamma);$$

$$\frac{\partial f}{\partial y} = y\{ -20\zeta x^3 - 12\epsilon x^2 + (20\zeta y^2 - 6\delta)x \\ + (4\epsilon y^2 - 2\beta) \};$$

$$\frac{\partial f}{\partial w} = -\frac{1}{K}.$$

These values do not lend themselves to an easy direct determination of the curves of equal shear force, but the values of the shear force along radial lines  $y=px$  are easily found, and the curves being plotted, the equal shear curves may then be drawn easily. The result for the section approximating to the valley of the Hintereis Glacier is given in the preceding paper, fig. 4; the curve  $d$  is the shear on the bed, and the curve  $e$  is the transverse surface shear.

\* Phil. Mag. July 1913, p. 109.

XVII. *On the Ionization in various Compounds of Carbon, Hydrogen, and Oxygen by homogeneous X-radiation. By H. MOORE, B.Sc., A.R.C.S., Assistant Lecturer in Physics at King's College, London* \*.

MANY investigations have been carried out by different observers, with a view to discovering the action of X-rays on compounds consisting of a small number of elements combined together in different ways. The results obtained have not in all cases been easy to understand, and the deductions made therefrom have been, in consequence, somewhat inconclusive. Where this has not been the case, certain conclusions may have been indicated, but the experimental results have not been sufficiently accurate to afford them very satisfactory support, or else the number of compounds used (consisting of the same two or three elements only) has not been sufficiently large to test these conclusions at all widely.

In most of these investigations the results have been complicated by the fact that a heterogeneous beam of primary X-rays has been used, the composition of which was probably different at different periods during the experiments; also an appreciable amount of the ionization produced has been due to secondary radiations from the sides of the ionizing chamber.

Some suggestion of an "additive" law is indicated by many of the results obtained, *i.e.* that the ionization is a property of the atom; while, however, this law seems to be approximately obeyed in many cases, there are, in others, deviations from it which are not to be explained by experimental errors, and it appears that the ionization also depends somewhat on the state of combination (Crowther, *Proc. Roy. Soc.* vol. lxxxii. A. p. 127).

The case of certain compounds of sulphur forms a notable exception to this atomic law, and the experiments of Barkla and Simons † show conclusively that the ionization is not purely atomic, but may be largely affected by the compound used, though the deviation is not large except in a few cases.

With a view to obtaining a large number of observations on different combinations of one small group of elements, the present experiments were confined entirely to compounds of oxygen, carbon, and hydrogen. In this way values for

\* Communicated by Prof. C. G. Barkla, F.R.S.

† *Phil. Mag.* Feb. 1912, p. 23.



"atomic" ionization or other "atomic" property (if such there be) can be determined from observations on two of the compounds (the effect of hydrogen being inappreciable) and these values tested by substitution in the other compounds. These calculated results can then be compared with the experimental observations, agreement or disagreement (within experimental error) indicating the existence of the law, or not.

To still further simplify matters, secondary homogeneous beams of X-radiation of definite hardness were used, the type of radiation used throughout the ionization experiments being the secondary radiation from copper.

A long cylindrical chamber was used, lined with aluminium and with aluminium ends, but it was found after a number of preliminary experiments, that the ionization due to radiation from the sides and ends (chiefly corpuscular) formed an appreciable proportion of the total ionization produced. This could have been allowed for with sufficient accuracy as it proved later, but the correction would have been unduly large in one or two cases. For this reason the preliminary results were discarded, and for the final experiments a lining of pure filter-paper was used inside the aluminium lining already referred to, the correction being thereby reduced to less than one-third of its previous value.

The observations given below were obtained with this paper-lined chamber; they differ in each case by an almost constant quantity from the preliminary results obtained, which shows that the correction, even without the paper lining, could have been made with reasonable accuracy, and also indicates the accuracy with which the various observations could be made.

After each experiment, the paper lining was renewed, as there was some difficulty in completely removing the last traces of the organic vapours used. On account of this difficulty, the observations on hydrogen were always carried out immediately after re-lining the chamber, the experiments on the vapour-mixture being carried out subsequently.

An electroscope attached to an axial electrode inside the chamber served to detect and measure the leak produced by ionization inside the chamber.

The method of experiment was to pass a mixture of hydrogen and the vapour employed into the chamber, the pressure of the vapour being its saturation pressure at  $0^{\circ}\text{C}.$ , while the total pressure was atmospheric. This mixture was then exposed to the homogeneous secondary radiation from copper, and the leak from the electroscope corresponding to the ionization produced was compared with that in a standard

electroscope exposed to the same radiator. By replacing the mixture with air, the ionization produced in air at 76.0 cm. by the same beam of rays could be measured immediately after the experiment with the mixture, the leak with air being compared with the same standard electroscope as before.

From these observations the ratio of the ionization in the mixture to the ionization produced by the same beam in air was calculated for each mixture used, these ratios being given in column II. Table I.

To determine what part of the ionization was due to the hydrogen in the mixture, separate experiments were performed as indicated above, using hydrogen alone at atmospheric pressure. The ionization in the hydrogen alone includes the effect of the corpuscular radiation from the ends of the chamber, and, deducting this from the total ionization produced in the mixture, the remainder gives the ionization due to the vapour alone at its saturation-pressure for 0° C.—at any rate as a first approximation. This method of calculation also eliminates any other constant error, such as insulation leak, &c.

The values for the relative ionizations in the hydrogen are given in column III. Table I., column IV. giving the ionization due to the vapour alone at its saturation-pressure at 0° C. in terms of the ionization produced by the same beam in air at atmospheric pressure. From the values tabulated in column IV. the ionizations which would be produced in the vapours alone at 76.0 cm. were calculated, assuming the ionizations to be proportional to the pressures: these are the numbers given in column V. of the same Table.

It was found impossible to obtain any “atomic” ionization values which would satisfy these observations at all accurately. Values for the ionizations due to an atom of carbon and to an atom of oxygen were obtained which would satisfy any two of the substances used, but when these values were substituted for in the molecular composition of any of the other vapours, the values obtained differed by as much as 25 per cent. from the observed values.

That the absorption and ionization produced in the same vapour at different pressures is proportional to the pressure—provided the variation in the secondary radiation escaping is negligible—has been amply shown by Crowther \*, Owen †, and others and therefore this method of calculation would have demonstrated the existence of “atomic” ionization if ionization had been truly atomic. The amount of secondary

\* Camb. Phil. Soc. Proc., Feb. 1909.

† Roy. Soc. Proc., May 1912.

TABLE I.

SUBSTANCE.	Vapour-pressure in cm. of Hg. I.	Ionization in Mixture (Air = 1). II.	Ionization due to H <sub>2</sub> , hydrogen, &c. (Air = 1). III.	Ionization due to Vapour (Air = 1). IV.	Calculated Ionization in Vapour at 76.0 cm. of Hg. V.
Methyl Formate . . . . .	19.0	0.500	0.0105	0.490	1.96
Ethyl Oxide (Ether) . . . . .	18.5	0.454	0.0105	0.444	1.92
Ethyl Formate . . . . .	7.25	0.198	0.0127	0.185	1.94
Methyl Acetate . . . . .	6.21	0.175	0.0130	0.162	1.98
Benzene . . . . .	2.65	0.060	0.020*	0.040	1.15
Ethyl Acetate . . . . .	2.43	0.082	0.014	0.068	2.23
Ethyl Alcohol . . . . .	1.27	0.027(6)	0.014	0.0136	0.81
Hydrogen . . . . .	76.0	0.014			

\* In the experiments on Benzene the paper lining of one end was omitted, the hydrogen value being 0.020, as against 0.014 in the other cases.

X-radiation from the ends and sides must have been very small, producing a correspondingly minute ionization, while, being very soft, it would be completely absorbed even in the case of hydrogen alone. Its effect was thus entirely eliminated in the process of calculation, or at any rate, any error due to it was reduced to something far below the errors of experiment.

Corpuscular radiation from the ends of the chamber was small in amount, and was liberated in all the experiments in equal amounts. The only error it could introduce would be negligibly small in most cases, depending on whether equal numbers of corpuscles produced equal ionizations in every case.

The corpuscular radiation from the gases and vapours in the ionizing-chamber was absorbed differently in the various experiments, however. In the mixtures containing the substances of higher vapour-pressure, it would be mainly absorbed by the vapour, but when compounds of low vapour-pressure were used, the corpuscles would be chiefly absorbed by the hydrogen. The ionization produced in a vapour is not necessarily the same as that produced in hydrogen, when equal numbers of corpuscles are absorbed in each—the ionization being usually larger in the vapour than in the hydrogen\*. The effect of this is that, in the mixtures containing a larger proportion of vapour, the ionization due to the corpuscular radiation from the mixture is greater than that which would be produced by the liberation (and subsequent absorption) of an equal number of corpuscles in the mixtures containing the low pressure vapours. The observed ionizations deviated from an "atomic" law in this kind of way, being relatively much higher in the higher pressure vapours than in the low pressure vapours, and accordingly it was in this direction that a further investigation was made.

The paper by Kleeman, to which reference has already been made, gave the ratio of the ionization produced in certain vapours alone, to that produced in air by the total absorption of equal quantities of corpuscular radiation. From these ratios it is possible to calculate the corresponding ratio for a *mixture* of gases or vapours, provided the relative amounts of corpuscular radiation absorbed by each of the constituents are known. The relative amounts absorbed by the vapour and by the hydrogen in the various mixtures were calculated assuming the absorptions to be proportional to the densities of the gases actually present (except for hydrogen which behaves anomalously). In this way calculations were made to determine how much corpuscular radiation must have been liberated in the various

\* Kleeman, Roy. Soc. Proc., March 1910.



mixtures in order to produce the observed ionizations, it being assumed for this purpose that the ionization due to X-rays is produced by the ejected corpuscles. The results obtained suggested that the true "atomic" phenomenon might be the amount of corpuscular radiation liberated, the final ionizations depending on the number of ions produced in the various vapours by the ejected corpuscles.

It was impossible to obtain data for all the vapours used, and therefore a fresh series of experiments had to be undertaken to obtain the required factors. These experiments were carried out on the mixtures themselves, the object being to find what ratio exists between the ionization produced in air to that produced in each mixture when equal quantities of corpuscular radiation are absorbed in each. By this means the amount of liberated corpuscular radiation corresponding to any observed ionization can be determined for each mixture. The direct determination of this factor for each mixture obviates any errors which might creep into its calculation (from Kleeman's numbers) based on a density absorption law, a law which is possibly not universally obeyed—hydrogen being a noteworthy exception.

In this second type of experiment, a short wide chamber was used, through which the homogeneous X-radiation from tin was passed. A reversible lining allowed two kinds of experiments to be made, one without, the other with corpuscular radiation. The lining consisted of thin card coated with gold-leaf on one side only. It was used with the gold outwards at first, when the amount of corpuscular radiation entering the chamber would be small; then, during the second kind of experiment it was reversed so that the gold was turned inwards, thus introducing a large number of corpuscles into the mixture. The X-radiation, having to pass through the same sheets of material in both cases, would be of the same intensity in the gaseous mixture, and the ionization due to the X-rays absorbed by the mixture would be identical in the two experiments. By deducting the ionization with the gold outwards from that with the gold inwards, the ionization produced in the mixture by the corpuscular radiation from the gold is given. A similar pair of experiments carried out with air instead of the mixture gives the ionization produced in air by the liberation of an equal amount of corpuscular radiation. By this method the required factors were obtained, experiments being also made with hydrogen alone to determine the factor for hydrogen: the factors obtained are given in column II. Table II.

TABLE II.

Substance.	Ionization in Mixture (Air=1). I.	"Corpuscular Factor" for Mixture (Air=1). II.	Corpuscular Radiation from Mixture (Air=1). III.	Corpuscular Radiation due to Hydrogen &c. (Air=1). IV.	Corpuscular Radiation from Vapour present (Air=1). V.	Calculated Corpuscular Radiation from Vapour at 76 cm. of Hg (Air=1). VI.
Methyl Formate .....	0.500	1.18	0.424	0.0108	0.413	1.64
Ethyl Oxide (Ether) ..	0.454	1.27	0.357	0.0108	0.346	1.42
Ethyl Formate .....	0.198	1.05	0.189	0.0131	0.176	1.84
Methyl Acetate .....	0.175	1.10	0.159	0.0134	0.146	1.79
Benzene .....	0.060	.99	0.061	0.0207*	0.040(3)	1.15
Ethyl Acetate .....	0.082	1.03	0.080	0.0144	0.0656	2.03
Ethyl Alcohol .....	0.027(6)	.98	0.028	0.0144	0.0136	.83
Hydrogen .....	0.014	.97(5)				

\* See footnote to Table I

It is possible now, on the assumption already referred to, to calculate from the ionizations observed the total corpuscular radiation liberated in each mixture by the X-ray beam used, this ionization being produced by the re-absorption of these ejected corpuscles. Thus if the ionization produced in a certain mixture (column II. Table I.) is divided by the factor corresponding to that mixture as given in column II. Table II., the result obtained is a measure of the total corpuscular radiation liberated in the mixture by the passage of the beam of X-rays; these results are given in column III. Table II. The corpuscular radiation from the sides of the chamber and from the hydrogen is obtainable from the corresponding observations on hydrogen alone, hence by deducting for each mixture the corpuscular radiation due to the hydrogen and from the sides, the corpuscular radiation liberated from the vapour present is obtained. The numbers in column IV. Table II. give the amount to be deducted in each case, being calculated on the assumption that this additional corpuscular radiation is entirely due to the hydrogen, none coming from the ends; this is, of course, untrue, but the error due to this is no larger than if it were assumed to be all from the ends, and in either case is beyond the limits of experimental accuracy. The corpuscular radiation liberated from the vapour alone at its saturation pressure for  $0^{\circ}\text{C}$ . is given for each vapour in column V. Table II.

Insulation and other constant leaks are not corrected for by this method with absolute accuracy as the "factors" are not exactly equal; as, however, these steady leaks were very small, and the "factors" are not very different from unity, these leaks are still corrected for to well below the limits of experimental accuracy, an important advantage of this method when the total ionization leaks in some cases are so very small.

Having obtained the values for the corpuscular radiation liberated from each vapour at a known pressure, the corpuscular radiation from each corresponding to a pressure of 76 cm. was calculated (column VI. Table II.).

Equations were then formed, giving the numbers of atoms of carbon, oxygen, and hydrogen in each compound, and equating their sum to the corpuscular radiation calculated as above for that compound.

Thus, if  $O$  represents the corpuscular radiation from an atom of oxygen,  $C$  that from an atom of carbon, and  $H$  that from an atom of hydrogen, we obtain the equations:—

Methyl Formate .....	$2 C + 4 H + 2 O = 1.64$
Ethyl Oxide (Ether) ...	$4 C + 10 H + O = 1.42$
Ethyl Formate .....	$3 C + 6 H + 2 O = 1.84$ (1.84)
Methyl Acetate .....	$3 C + 6 H + 2 O = 1.79$ (1.84)
Benzene .....	$6 C + 6 H = 1.15$ (1.20)
Ethyl Acetate .....	$4 C + 8 H + 2 O = 2.03$ (2.04)
Ethyl Alcohol .....	$2 C + 6 H + O = 0.83$ (1.00)

In each case the effect of hydrogen can be neglected, and two equations suffice to obtain values of  $O$  and  $C$ , the "atomic" corpuscular radiations.

The equations chosen are those for ether and methyl formate on account of the much greater experimental accuracy obtainable in these cases, due to the larger pressures used, and consequent larger ionizations obtained.

These equations give values:  $O=0.62$ ,  $C=0.20$ .

On substituting these values in the other equations, the values given in brackets are obtained, the agreement being remarkably close in some cases, and well within the limits of accuracy expected in all cases except that of alcohol.

The discrepancies in the cases of benzene and alcohol were expected to be much greater than in any others, as the total ionizations obtained were extremely small, being less than  $\frac{1}{30}$  that of air. Of this, about 50 per cent. was due to corpuscular radiation from the sides and from the hydrogen, so that the corrections amounted to half the total ionization observed.

In order to obtain accurate results, the mean of ten observations was taken in each case, but even with this precaution, an error of 5 per cent. of the whole ionization was reckoned possible, which is equivalent to a 10 per cent. error on the result.

The smallness of the ionizations in these two cases is partly due to the low molecular weight of these compounds (and to the absence of oxygen from the benzene molecule), but is chiefly due to the low pressures used. In the case of ethyl acetate, the low vapour-pressure at  $0^{\circ}$  C. is made up for to a great extent by the high molecular weight and the large proportion of oxygen in the molecules, hence the observations on ethyl acetate were much more accurate than those on benzene and alcohol.

The agreement obtained between the two values for



benzene, the one calculated from observations, the other on the assumption that the emission of corpuscles is an "atomic" phenomenon, is thus well within the limit of experimental error considered possible, but the difference between the values for alcohol requires some further explanation.

In all the other cases, the purest chemicals supplied by Kahlbaum were used, but pure alcohol could not be obtained on account of Excise regulations; the alcohol used was ordinary "absolute" alcohol, and probably contained 1-2 per cent. of water. The presence of a very small quantity of water would reduce the saturation vapour-pressure to below that of pure alcohol, and at 0° C., a difference of 1 mm. in the pressure would cause an error approaching 10 per cent. This, together with the error rendered possible by the very small ionization values already discussed, would probably account for the large discrepancy between the two alcohol values.

The values for the corpuscular radiation from an atom of oxygen and an atom of carbon, obtained from these equations, may be substituted in the molecular formula for other gases and vapours not experimented with in the present series of observations. The numbers thus obtained, when multiplied by the "corpuscular factor" for the gas or vapour used, should give the ionizations produced in these gases or vapours at 76.0 cm. by a stream of homogeneous (copper) X-radiations in terms of that produced by the same beam of radiation through an equal length of air at 76.0 cm.

Thus, in the case of oxygen, the amount of corpuscular radiation liberated would be 1.24 times that liberated in air, taking the "atomic" value = 0.62 as obtained from these equations. The "corpuscular factor" for oxygen being 1.10 (Barkla & Philpot, *Phil. Mag.*, June 1913), the ionization in oxygen as compared with that in an equal length of air should be 1.36 for copper X-radiation. The value actually obtained by these observers is 1.38.

In carbon di-oxide the corpuscular radiation would be  $0.2 + 1.24 = 1.44$ . The corpuscular factor obtained by Kleeman is 1.08, giving an ionization of 1.56 compared with air, the experimental values of Crowther & Owen being 1.57 (Crowther, *Cambridge Phil. Soc.*, Feb. 1909; Owen, *Roy. Soc. Proc.*, May 1912).

*Conclusions.*

It has been shown (Barkla & Simons, *Phil. Mag.*, Feb. 1912) that the relative ionizations produced by equal absorptions of Röntgen rays in various gases are the same (within limits of experimental error) as those produced by total absorption of corpuscular radiation excited by X-rays. This important result indicated the possibility of ionization by X-rays being due entirely to the resulting corpuscular radiation—a conclusion which was indeed stated more definitely by Bragg. Subsequent work has supported this indication, and the condensation experiments of C. T. R. Wilson (*Roy. Soc. Proc.*, June 1912) seem to have put the matter beyond doubt. If this is the case, and it is now supported by ionization experiments, it would appear from the present experiments that the real atomic effect is the liberation of corpuscles from the atoms, accompanied, of course, by an absorption of the X-ray beam, which would also be “atomic,” *i. e.*, it would appear that the number of corpuscles liberated from an atom by a beam of X-rays is the same whether the atom is in combination or not, the ionization produced being a secondary effect, the result of the absorption of this liberated corpuscular radiation by the gas.

This conclusion is in agreement with the conclusions arrived at as a result of previous work on this subject, *viz.*, “Ionization by Röntgen radiation is approximately atomic, but depends somewhat on the chemical combination of the elements.”

Apparently the corpuscular radiation obeys an “atomic” law, and the ionization is approximately “atomic” because the “corpuscular factor” is rarely very different from unity. Of course, the present experiments have been limited to elements of low atomic weight, which according to established laws give off only a very weak secondary characteristic X-radiation when exposed to X-rays of ordinary penetrating power. There is, however, no apparent reason for doubting their complete generality.

I should like to express my great indebtedness to Professor Barkla whose suggestions and advice have been invaluable throughout the whole of these experiments.

XVIII. *Note on the Heat of Formation of Hydrogen from Hydrogen Atoms.* By IRVING LANGMUIR, Ph.D., General Electric Co., Schenectady, N.Y.\*

DR. N. BOHR, in his recent valuable and wonderfully suggestive paper on the Constitution of Atoms and Molecules (Phil. Mag. xxvi. p. 863, 1913), calculates the heat of formation of hydrogen molecules from the atoms to be 60,000 calories per gram-molecule. He points out that this value is "considerably less than the value of 130,000 found by Langmuir (Journ. Amer. Chem. Soc. xxxiv. p. 860, 1912) by measuring the heat-conduction through the gas from an incandescent wire in hydrogen."

In order that the results obtained by me may not bear false evidence against the beautiful theory derived by Dr. Bohr, I take this opportunity of giving a preliminary account of some more recent measurements carried out by Mr. G. M. J. Mackay and myself, on the dissociation of hydrogen.

The method adopted was similar to that previously used, namely, to determine the heat-loss from electrically heated tungsten wires in hydrogen. In these experiments, however, very much greater care was used in determining the temperatures of the wires and in obtaining extremely pure hydrogen. Pressures of hydrogen ranging from 1 mm. up to 760 mm. of mercury were used. Still further experiments which, however, have not yet been completed, were made at pressures from 0.01 mm. up to 20 mm. pressure.

The measurements at low pressures gave very interesting results, namely, that at about one-tenth of an atmosphere pressure of hydrogen, the total heat-loss from filaments heated to very high temperatures (3000° K.) is several times as great as in hydrogen at atmospheric pressure.

By subtracting the heat-loss due to *normal* heat-conduction from the *total* observed heat-loss, the heat carried by diffusion of hydrogen atoms is obtained. By plotting the logarithm of this quantity against the reciprocal of the absolute temperature, straight lines are obtained in each experiment. The slopes of all these lines are practically equal, no matter what pressure of the hydrogen was used (above 10 mm.).

On the assumption that the diffusion coefficient varies with the  $3/2$  power of the temperature, this leads to the result that the heat of formation of hydrogen is about 76,000 calories per gram-molecule, as against 130,000 previously found. The reason for the high value of the latter figure is, that it was

\* Communicated by the Author.

based on a calculation of the actual value of the diffusion coefficient of hydrogen atoms through ordinary hydrogen. The present results show that the actual degree of dissociation is much smaller than that previously found, and that even at  $3500^{\circ}$  K. hydrogen is probably not dissociated to a very great extent. It is hoped that the experiments at very low pressures will make possible a quantitative estimation of the degree of dissociation.

In conclusion, the writer wishes to point out that the value of 130,000 calories referred to by Bohr is undoubtedly too high, and that the experimental evidence now indicates a value of about 75,000 to 80,000 calories. That the correct value, however, is as low as the 60,000 calculated by Bohr seems very improbable.

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XIX. *Heating Effects at the Anode in Vacuum-Tubes.* By B. HODGSON, M.Sc., Ph.D., Assistant Lecturer in Physics, The University, Bristol\*.

§1. **I**N a previous communication† the author showed that the energy communicated to the anode during discharge in air was approximately proportional to the current through the tube. The experiments were made with gas-pressures 2·7, 1·05, and 0·63 mm. The experiments to be described have been carried out over a large range of currents and pressures in oxygen. The apparatus used was that described in earlier papers‡. The method of experimenting was slightly altered. Instead of allowing the anode to rise to that temperature at which the loss of energy by radiation was equal to the gain from the bombardment of negative carriers, the rise in temperature in a definite interval of time was measured and a correction for loss by radiation applied. This method was found to yield results much more quickly with only a small loss in accuracy. The anode used was of lead, and had a heat capacity of 2·2 gm. calories.

§ 2. *Experimental Results.*

The results in Table I. show the heat energy received by the anode in one second for currents varying from 0·001 amp. to 0·007 amp. and pressures between 3·8 mm. and

\* Communicated by the Author.

† Hodgson, Phil. Mag. xxv. p. 458 (1913).

‡ Hodgson, Phil. Mag. xxv. p. 453 (1913); Hodgson & Mainstone, Phil. Mag. xxvi. p. 411 (1913).



0.18 mm. of mercury. The quantities given yield ergs if multiplied by  $10^4$ .

TABLE I.

<i>i</i> amps.	·001	·002	·003	·004	·005	·006	·007
Pressure							
mm.							
3.8	...	75	99	124	146	197	222
3.08	...	75	110	132	163	...	...
2.25	35	73	102	131	172	211	...
1.5	70	138	194	258	312	362	402
1.33	69	128	186	248	299	346	399
1.21	66	120	181	234	289	349	418
1.10	63	115	154	217	272	321	364
1.00	63	110	166	200	266	311	356
0.81	56	102	152	199	249	289	348
0.60	49	96	135	190	220	260	281
0.50	48	90	119	150	145	157	127
0.41	38	69	69	50	44	59	96
0.35	34	17	28	43	74	121	330
0.28	12	21	61	196	576	—	—
0.23	27	218					
0.18	83						

The corresponding values of the potential (V) between the electrodes of the vacuum-tube are given in volts in Table II.

TABLE II.

<i>i</i> amps.	·001	·002	·003	·004	·005	·006	·007
Pressure							
mm.							
3.8	...	565	515	502	490	490	510
3.08	630	527	505	490	487	517	—
2.25	560	530	520	530	527	542	—
1.5	660	655	660	650	650	652	640
1.33	647	632	652	647	635	640	642
1.21	620	627	632	647	650	647	650
1.10	617	627	635	647	650	655	657
1.00	612	625	642	643	632	637	640
0.81	597	635	655	675	680	680	680
0.60	663	660	702	740	777	807	830
0.50	627	720	787	848	872*	950*	980*
0.41	672	777	855*	940*	1075†	1230†	1500§
0.35	750	885	1000†	1210†	1300†	—	—
0.28	940†	1260†	1560§	2200§			
0.23	1700§	3100§					
0.18	2750§						

These potential differences were measured by means of a Braun electrometer. The asterisks and other signs following some of these quantities denote the type of discharge occurring in the tube. With high pressures there appears on the anode, the anode glow which is succeeded by a dark space and the faintly luminous positive column. In this case no distinguishing sign follows the values of  $V$ . Then as either the current increases or the pressure decreases, the positive column contracts towards the anode till only the surface of the anode is illuminated. This condition is denoted by the asterisk \*. Then as the pressure decreases further, the anode glow disappears, and except for the negative glow, no luminosity appears in the tube. This condition occurred only once—with a current of 0.002 amp., and a pressure of 0.35 mm. As the vacuum becomes more perfect, there appears a hazy luminosity throughout the tube, without any glow on the anode. This condition is denoted by the sign †. Finally, the luminosity in the tube increases in brightness, and there is cast behind the anode a shadow, which becomes more definite as the pressure is reduced. The sign § marks this stage.

Tables III. and IV. give other results for the energy ( $M\theta$ ) given to the anode per second for constant current 0.003 amp. at various pressures.

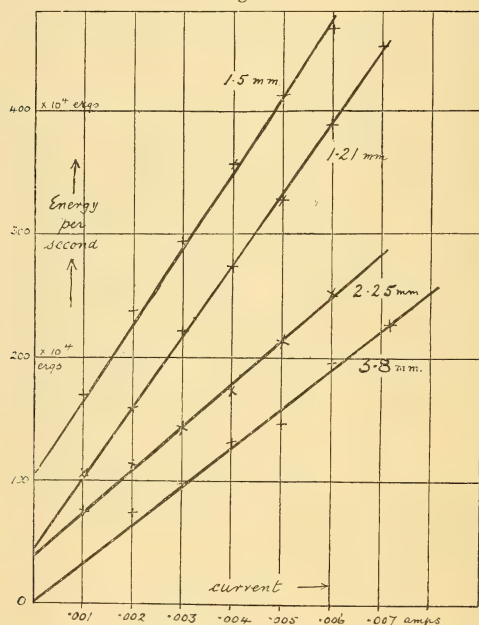
TABLE III.

TABLE IV.

Pressure (mm. Hg).	$M\theta$ ( $10^{-4}$ erg).	Pressure (mm. Hg).	$M\theta$ ( $10^{-4}$ erg).
1.75	175	4.80	130
1.75	186	3.36	106
1.48	183	2.85	110
1.25	175	2.52	120
1.00	167	2.19	113
0.94	159	1.80	129
0.94	157	1.62	134
0.73	146	1.40	177
0.62	129	1.27	159
0.41	86	1.15	174
0.26	26	1.03	163
0.16	202	0.92	167
		0.85	160
		0.67	143
		0.46	85
		0.32	25
		0.24	34
		0.20	57
		0.15	197

Fig. 1 shows four results taken from Table I. Three of the curves are moved bodily upwards for the sake of clearness. Energy supplied to the anode per second is plotted

Fig. 1.

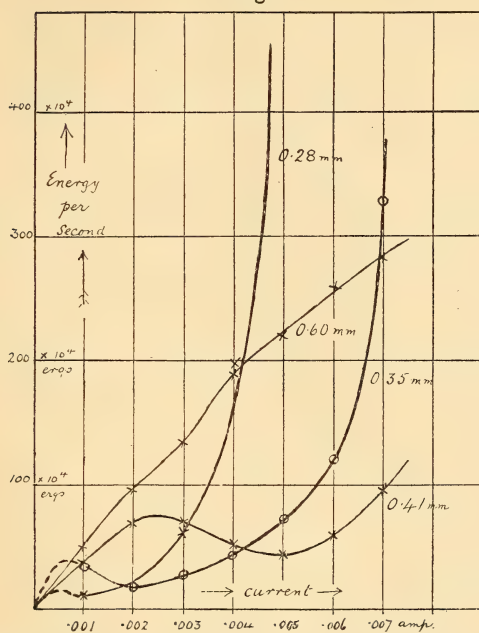


against current for constant pressure. A linear relation exists at the pressures used. For lower pressures the curves are of a different type, and fig. 2 gives some of these, which all possess the same general shape. For small currents proportionality exists between current and energy, and then as the current increases the energy communicated to the anode actually decreases and falls to a minimum value, after which a quick rise is obtained. For currents smaller than 0.001 amp. no values were obtained, but the probable courses for the 0.28 mm. and the 0.35 mm. curves are shown by the dotted parts. The curves in fig. 1 would probably show the same form could currents large enough be obtained.

If certain assumptions be made, the average energy per ion can be obtained. If  $n$  negative carriers with only one charge strike the anode per second and do not ionize there, then  $ne=i$ , where  $i$  is the current and  $e$  the charge per ion. Then the energy given to the anode per second is  $neV'$  where  $V'$  is the mean potential through which the ion falls, and

$$neV' = iV'.$$

Fig. 2.



If, then, the results in Table I. are divided by the current the average voltage fall per ion is obtained. This is given in volts in the following table :—

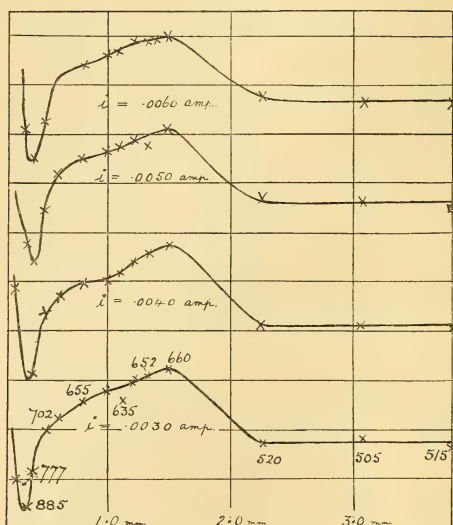
TABLE V.

<i>i</i> amps.	·001	·002	·003	·004	·005	·006	·007
Pressure. (mm.).							
3.80	59	37	33	31	29	33	—
3.08	55	37	37	33	33	33	—
2.25	35	36	34	33	34	35	—
1.50	70	69	65	65	63	60	57
1.33	69	64	62	62	55	58	57
1.21	66	60	61	59	58	58	60
1.10	63	58	51	54	55	54	52
1.00	63	55	56	50	53	52	51
0.81	56	51	51	50	50	48	50
0.60	49	48	45	45	44	43	40
0.50	48	45	40	38	29	26	18
0.41	38	35	23	12	8	10	14
0.35	34	8	9	11	15	20	47
0.28	12	10	20	49	115		
0.23	27	109					
0.18	83						



If now  $V'$  is plotted against pressure with constant current the curves shown in fig. 3 are obtained. They show also the

Fig. 3.



relation between pressure and energy received per second, the scale being in this case different for each curve. Five additional curves, similar in shape, can be got from Tables III., IV., and V. They all show a pressure range from 2 to 4 mm. in which the energy given to the anode is approximately constant. As the pressure is reduced the energy per ion increases to a maximum at about 1.5 mm. pressure. It then falls to a minimum whose position and value vary with the current, and after this minimum a rapid rise is obtained for lower pressures.

### § 3. *Theoretical Conclusions.*—I. *The Large Heating Effect.*

From Table I. it will be seen that the energy communicated to the anode per second for a current of 0.003 amp. was practically constant and equal to  $100 \times 10^4$  ergs for pressures between 2 and 4 mm. This is equivalent to an average ionic energy of 35 volts (Table V.), assuming that the ions do not ionize at the anode surface. It is easy to show that this energy cannot be acquired by the ion in its mean free path. The anode fall is about 20 volts, and this fall occurs quite close to the anode, so close that a sound

cannot be got near enough to the anode to measure the distance in which this voltage drop occurs. Now the mean free path of an electron in oxygen at 3 mm. pressure is about  $1.4 \times 10^{-2}$  cm., and as the potential gradient in the positive column is small, the maximum energy that an electron can acquire in moving up to the anode from a point distant  $1.4 \times 10^{-2}$  cm. is the energy of the anode fall at most, *i. e.* a 20-volt energy. As the measured energy is 35 volts, a 15-volt energy must be accounted for in some other way.

Now a rough value of the potential gradient in the positive column can be got from a knowledge of the cathode fall, the anode fall, the potential across the tube, and the distance between the electrodes. In the case considered, the mean gradient in the positive column

$$\begin{aligned} &= \frac{515 - 370}{10} \frac{\text{volt}}{\text{cm.}} \\ &= 15 \frac{\text{volt}}{\text{cm.}} \end{aligned}$$

If, then, we assume that all the energy acquired by the negative carriers in moving up to the anode from a distance of 1 cm. is given up as heat, all the 35-volt energy is accounted for.

Now in 1 cm. at this pressure, a corpuscle makes about 50 collisions and an ion of molecular size about 200, so that in spite of a great number of collisions energy is "accumulated" by the negative carriers in some way and transferred to the anode. It is not suggested that all the energy acquired by the carriers within 1 cm. of the anode is transferred to the anode, and none from the positive column beyond this distance. Probably the whole column of gas up to the negative glow contributes to the 15-volt energy not accounted for by the anode fall.

## II. Possibility of an "Accumulation" of Energy.

The following considerations show the possibility of an "accumulation" of energy by an ion in spite of frequent collisions.

One possibility—that ionization occurs on collision—may be regarded as very improbable, because the gradient in the positive column is small.

A further possibility is that an aggregate ion or cluster is formed on collision. There is abundant evidence to show

that clusters and multiple-charged atoms both exist. H. A. Wilson found that the mobility of ions in flames changed suddenly at a certain temperature, suggesting a change in the clustering of the ions. Todd \* has proved, from measurements of the mobility of the positive ion at fairly low pressures, the existence of clusters up to cluster 6 in Kleeman's notation †, and also ‡ that the negative ion consists of a cluster which becomes less complex at lower pressures.

Lattey and Tizard § have obtained evidence of the existence of a cluster of 25 molecules round a positive charge.

Kleeman || has shown from theoretical considerations that there probably exists in ionized gases a continual forming and breaking up of clusters of different orders so that a state of equilibrium is finally reached, in which the number of clusters of different orders depends on the electric field and the gas pressure.

Now it can be shown that the formation of clusters permits the "accumulation" of energy. Consider a cluster  $n$ , i. e.  $n$  molecules aggregated round one charge, colliding with another molecule and forming a cluster  $n+1$ , the collision being direct. Let the mass, energy of motion, and velocity of cluster  $n$  just before collision be respectively

$$nm, E_n \text{ and } v_n,$$

and let these quantities for cluster  $n+1$  immediately after collision be  $\overline{n+1} m$ ,  $E_{n'}$ , and  $v_{n'}$ .

Then

$$nm v = \overline{n+1} m v_{n'}$$

or

$$v_{n'} = \frac{n}{n+1} v_n.$$

Hence

$$E_{n'} = \frac{1}{2} \overline{n+1} m \left( \frac{n}{n+1} \right)^2 v_n^2.$$

Now

$$E_n = \frac{1}{2} n. m. v_n^2,$$

therefore

$$E_{n'} = \frac{n}{n+1} E_n.$$

That is the energy of motion of the cluster just after

\* Todd, Phil. Mag. xxv. p. 165 (1913).

† Kleeman, Proc. Camb. Phil. Soc. xvi. p. 285 (1912).

‡ Todd, Proc. Camb. Phil. Soc. xvi. p. 21 (1912).

§ Lattey & Tizard, Proc. Roy. Soc. lxxxvi. A. p. 356 (1912).

|| Kleeman, Proc. Camb. Phil. Soc. xvi. p. 285 (1912).

collision is  $\frac{n}{n+1}$  of its energy immediately before, and the

larger the colliding cluster the smaller the fraction of energy not appearing as energy of motion. The latter fraction,

$\frac{1}{n+1} E_n$ , probably appears as internal energy of the cluster.

In some such way as above indicated, the energy is absorbed by the cluster till such amount is accumulated as to render it unstable. Now if it be assumed that the energy acquired per mean free path is the same for all clusters, an approximate value of the energy of cluster  $n$  after the  $n$ th collision can be

shown by induction to be  $E_n = \frac{n+1}{2} E_1$  where  $E_1$  is the

energy gained per mean free path. Now in the case considered above, a 15-volt energy has to be "accumulated," that is, all the energy available in a path 1 cm. long. As this would involve at least 100 collisions, and imply the formation of a cluster 100, it is improbable that the explanation of the phenomena is as simple as above described. It is clear that, in addition to collisions between clusters and molecules, there will be collisions among the clusters themselves. Once a cluster is formed, its acceleration in the electric field is less than that of the simple ion. So that it is possible for an ion or small cluster to overtake a larger one. In this case combination may take place resulting in a heavier cluster with increased energy, or two clusters if the resulting combination happened to be unstable. The accumulation of energy by the clusters will then reach some limit which depends on the number of complex ions of different orders in equilibrium under the conditions of the experiment. In addition to the energy of motion, some fraction of the energy absorbed by the clusters will also be given up to the electrode as heat.

Another explanation of the "accumulation" of energy suggests itself. The charged ion moving towards the anode gains energy in its mean free path, so that after collision with a neutral molecule, the latter rebounds with a greater momentum than it would possess if no current were flowing. This would be repeated after the ion had moved again in the electric field, so that there would be a transference of momentum along the tube towards the anode. This would mean that both a pressure and temperature gradient would exist in the positive column, and on this explanation the excess energy given to the anode would be accounted for by a transference of energy to the anode from a hotter gas surrounding it.

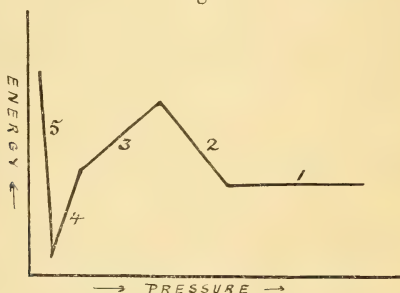


§ 4. *Discussion of fig. 3 Curves.*

These curves can be analysed into five distinct parts as shown in the diagram below.

The energy given up to the anode is constant for pressures above 2 mm. as shown in part 1 of fig. 4. At 2 mm. the energy begins to increase and reaches a maximum at a pressure of 15 mm. for all curves. The potential gradient

Fig. 4.



in the tube has also risen. In both parts 1 and 2 of fig. 4 the factor determining the energy appears to be the mean gradient in the tube, for in part 1 both gradient and energy are constant and a fixed ratio appears to hold between gradient and energy for points on parts 1 and 2. This is shown in Table VI. from results collected from Tables I. and II.

TABLE VI.

<i>i.</i>	<i>pr.</i>	Energy.	Gradient.	Gradient/Energy.
·002	{ 3·8	75	195	2·6
	{ 1·5	138	285	2·1
·003	{ 3·8	99	145	1·5
	{ 1·5	194	290	1·5
·004	{ 3·8	124	132	1·1
	{ 1·5	258	280	1·1
·005	{ 3·8	146	120	0·82
	{ 1·5	312	280	0·90
·006	{ 3·8	197	120	0·61
	{ 1·5	362	282	0·78
·007	{ 3·8	222	140	0·63
	{ 1·5	402	270	0·67

This implies that the ionization processes are constant over parts 1 and 2, the change in energy being due to changes in mobility of the ions and perhaps in the clustering.

By referring to Table II. it is seen that the voltage across the tube was always about 660 volts at 1.5 mm. pressure when the curve changes abruptly. The voltages actually registered were 660, 650, 660, 650, 652, and 640 volts. The sharp change in the curve is probably occasioned by the commencement of ionization in the positive column. The constant voltage across the tube at this point also suggests that the gradient has become large enough to effect ionization by collision. This ionization reduces the anode energy in two ways. In the first place ions are now travelling in both directions, and collisions can reduce considerably the energy of those moving towards the anode, and in the second place the bombarding negative ions may combine with the free positive ions and cease to have any acceleration in the electric field. Additional evidence of ionization is shown by the decrease in "resistance" of the tube. The potential across the tube is slightly below that in the initial part of section 3 (fig. 4). (For actual values of the potential across the tube see Table II.)

Part 4 (fig. 4) commences at a pressure of 0.5 mm. At this point the energy diminishes rapidly, probably owing to ionization at the anode surface. Here the current is no longer represented by  $i = ne$ ,

but by  $i = ne + n_1e$ ,

where  $n_1$  is the number of positive carriers produced per second at the anode ; so that the number of bombarding ions is reduced from

$$n \text{ or } \frac{i}{e} \text{ to } \frac{i}{e} - n',$$

which number reaches a minimum when  $n = n_1$ , *i. e.* when each negative ion sets free a positive ion on striking the anode. It is, then, possible for the lessening number of bombarding ions, aided by the motion of positive ions in the opposite direction, to give up less energy to the anode in spite of the increased gradient. When the minimum number of negative ions is obtained, further reduction in pressure produces an increase in the gradient in the tube, and hence an increase in the energy given up. This part is represented by the sharply rising part 5 (fig. 4).

These hypotheses lead to a fuller explanation of the discharge in vacuum-tubes. Suppose the gas pressure is large,

say 3-4 mm. in oxygen, and the current small enough to give a normal cathode fall. Although ionization is necessary at the cathode surface to make the current continuous \*, the author † has shown that only a small fraction of the bombarding ions produce fresh ions at the cathode surface. The relatively few corpuscles produced soon acquire energy in the cathode dark space sufficient to ionize many times. This energy is expended in the process of ionization in the cathode dark space and the negative glow. The corpuscles produced in the dark space soon produce fresh ions there, and so a progressive ionization occurs as the negative glow is approached. The increase in the number of ions per cm. reduces the gradient, and in the negative glow the "resistance" of the gas there is so small, that the gradient is negligible compared with that in the dark space; and when the electrons or negative ions have expended the energy acquired in the cathode dark space, no further ionization occurs. The formation of clusters begins, and these negative carriers drift in the electric field towards the anode. The hazy glow at the anode may be the result of ionization, but this must be due to only a small fraction of the bombarding ions. Otherwise the shape of the curve in fig. 4 is difficult to account for. As the pressure is reduced the phenomena occur as already described.

The curves in fig. 2 are explained in a similar way to those in fig. 3, as they represent the facts of Tables I. and II. is a different form, namely, with constant pressure instead of constant current.

#### §5. *Effect of Distance between the Electrodes on the Energy given to the Anode and Cathode.*

A tube was arranged so that one electrode was movable. The distance between the electrodes could be varied between 0 and 30 cm., and this process could be performed by using a winding arrangement without impairing the vacuum.

Though it was not possible to decide the relative values of the two suggestions in §3, the results are not in discord with either view. During the experiment the current and gas pressure were kept constant, and the distance between the electrodes and the energy given up to cathode or anode were measured. In the case of the cathode, the energy given up was independent of the length of the positive column except

\* J. J. Thomson, 'Conduction through Gases,' ii. ed. p. 585.

† Hodgson, Phil. Mag. xxvi. p. 460 (1913).

when the distance between the electrodes was so small that the nearness of the cool anode kept the cathode temperature low. With the anode the energy given up increased continuously with the length of the positive column.

The results are shown in the following Table :—

TABLE VII.

Lead Cathode in Oxygen.

$i = 0.0030$  amp.

$pr = 2.8$  mm. Hg.

$L$  = distance between electrodes (cm.).

$\theta$  = rise in temperature per minute ( $0^\circ$  C.).

L.	$\theta$ .	L.	$\theta$ .
0.3	6.15	8.10	7.15
0.3	6.20	10.7	7.00
0.65	6.50	13.8	7.10
0.65	6.85	17.5	6.90
0.70	6.80	22.2	7.05
0.70	6.50	25.8	7.10
1.80	6.90	29.8	7.02
1.80	7.05		

TABLE VIII.

Lead Anode in Oxygen.

$i = 0.0050$  amp.

$pr = 3.6$  mm. Hg.

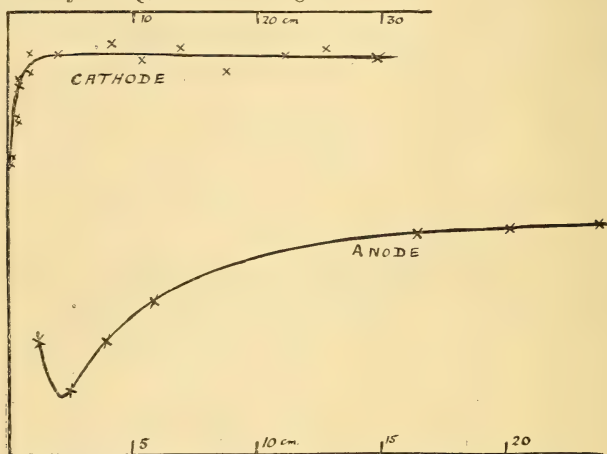
L.	$\theta$ .
24.1	14.2
20.1	14.1
16.5	14.0
5.9	12.6
4.0	11.8
2.5	10.8
1.3	11.8

$\theta$  here represents the equilibrium temperature of the anode under the above conditions, *i. e.* the temperature the anode rises to after a long interval of time. This method is more sensitive, for the rise in temperature per minute is only



small. The results of Tables VII. and VIII. are shown graphically in fig. 5.

Fig. 5.



In both curves with short distances, a disturbance is introduced due to the nearness of the electrodes. Neglecting these distortions, it is clear that the energy given up to the cathode is independent of the length of the distance between the electrodes. This agrees with the assumption made before that the bulk of the positive ions originate in the negative glow. Were any produced in the space nearer the anode, the energy given up would increase with the distance between the electrodes.

In the case of the anode an increase in the distance between the electrodes is accompanied by an increase in energy. Though the curves obtained showed a tendency to reach a maximum, none was reached even with a length of discharge of 24 cm. This seems to indicate that the transference of momentum by collision plays a large part in the "accumulation" of energy, for one would expect an equilibrium stage in clustering to be reached long before all the collisions in a 20 cm. path have occurred.

#### *Summary.*

1. Results showing the relation between current, gas pressure, and energy, given to the anode in oxygen have been obtained.
2. The relation between the energy communicated to either electrode and their distance has been investigated.
3. The mechanism of discharge has been discussed in the light of these results.

Physics Department,  
The University, Bristol.

XX. *On the Application of Graphical Methods to the Solution of Problems on Struts and Tie-Rods with Lateral and Non-Axial Loads.* By CECIL H. LANDER, M.Sc., A.M.Inst.C.E., Lecturer in Civil Engineering in the University of Manchester\*.

EXCEPT in the most simple cases considerable difficulties present themselves in the determination of stresses in struts and tie-rods which are subjected either to non-axial or to lateral systems of loading. If the bending moment at the point and the direct thrust in the column are known, the intensity of stress at any point can be calculated from the expression

$$f = \frac{My}{I} + \frac{P}{A}$$

where  $M$  = Bending moment at section considered ;  
 $I$  = Moment of inertia at that section ;  
 $y$  = Distance of the point from the neutral axis ;  
 $P$  = Direct thrust ;  
 $A$  = Area of section.

The direct thrust is always known, and the stress due to this can therefore be obtained with no further difficulty. With regard to the bending moment, however, matters are complicated by the fact that owing to the deflexion caused by the lateral loading, the moment will be increased in amount by the presence of the end load which in its turn again increases the deflexion, and so on until a balance is obtained.

For simple cases † expressions can be obtained which will give the actual bending moment at any point in the beam. A useful approximate method, suggested by Professor Morley ‡, consists in first calculating the central deflexion due to the lateral load alone, and then increasing the moment by an amount equal to the product of the end load and this deflexion. The reader is referred to Professor Morley's paper in which he shows that the error involved in most practical cases is negligible.

When, however, the lateral loading is complicated by the existence of several concentrated loads, due to the end load being non-axial or to a distributed lateral load of non-

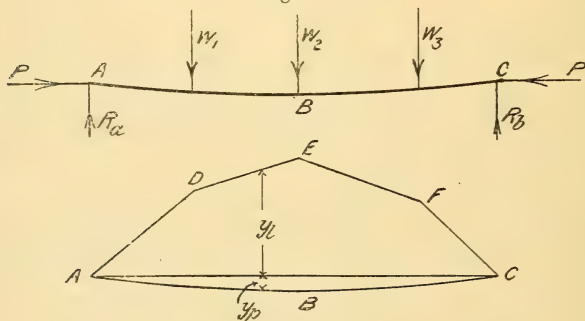
\* Communicated by Prof. J. E. Petavel, F.R.S.

† Perry, J., "Struts with Lateral Loads," Phil. Mag. March 1892.

‡ Morley, A., "Laterally Loaded Struts and Ties," Phil. Mag. June 1908.

uniform intensity such as that caused by the inertia of an engine connecting-rod, the following graphical methods present many advantages over analytical determinations. They are simple in application and, moreover, the error caused by any approximations can be readily estimated. In cases where beams are continuous over several supports, and have endlong loads applied, as for example the spars of aeroplanes, analytical expressions although obtainable are very difficult in application.

Let A, B, C (fig. 1 *a*) represent the centre line of a strut which is subjected simultaneously to an end load and to any system of lateral loading. Let the curve ADEFC (fig. 1 *b*) be the bending moment diagram for the lateral

Fig. 1 *a*.Fig. 1 *b*.

loads acting alone. The bending moment diagram due to the load P is given by the shape of the distorted column, that is by the curve ABCA. The total bending moment on each section is then given by the sum of the ordinates, that is  $y_l + y_p$ ,  $y_p$  being taken to the proper scale.  $y_l$  is already known, and it remains therefore to determine  $y_p$  the deflexion of the column at any point due to both loadings acting together.

The deflexion curve of a beam can be drawn if the bending moment diagram is known since the deflexion curve is the funicular polygon of the bending moment curve. Taking a beam under any loading, the method consists in first drawing the bending moment diagram for the lateral system acting alone. Now treat this diagram as if it were a curve showing load intensity at any point of the beam, and draw the bending moment diagram for this load intensity curve. We shall now have obtained a figure which will be such that its ordinates when divided by  $E \times I$  will give the deflexions due

to the lateral system acting alone. For the present purpose let us call this the primary deflexion diagram. If we now multiply the ordinates of this primary deflexion diagram by the end load  $P$ , we shall obtain a curve which will give the bending moment that would be produced if the ultimate curve of the strut under both lateral and end systems corresponded exactly to the shape of the primary deflexion diagram. A second approximation to the correct curve may be obtained by treating this additional or secondary bending moment curve in exactly the same manner as we previously treated the bending moment curve due to the lateral system acting alone. The secondary deflexion so obtained is usually unimportant but produces bending moments of small amount which may be added to those already found. By continuing the process we should finally arrive at a curve which would represent, within the limit of accuracy possible in graphical work, the exact shape of the bended strut. As the end-long load increases in magnitude and approaches the value given by Euler's formula for the crippling of a strut having no lateral loading, the effects of the secondary and higher deflexion curves become of great importance. For practical purposes of design, however, it will usually be found sufficiently accurate to take the total bending moment as being that due to the lateral loads plus that moment caused by the end loads acting through distances corresponding to the ordinates of the primary deflexion diagram. The degrees of accuracy may be judged by comparing the maximum ordinate of the lateral load bending moment diagram with that due to the primary deflexion diagram. It will usually be found that the latter is not more than one tenth the former, from which it is justifiable to assume that the maximum ordinate of the bending moment diagram due to the secondary deflexion curve would again be less than one tenth that of the primary deflexion diagram bending moment curve. The error involved by neglecting secondary deflexion curves would therefore be less than one per cent.

If the end load acts non-axially then the initial bending moment curve will be increased by an amount equal to the product of the end load and the initial eccentricity, and it will be necessary therefore to add a constant ordinate equal to this to the bending moment curve for the lateral system before drawing the primary deflexion curve. After this the work may be proceeded with exactly as before.

In the case of tie-rods under lateral loadings the bending moment diagrams obtained from the primary, etc. deflexion

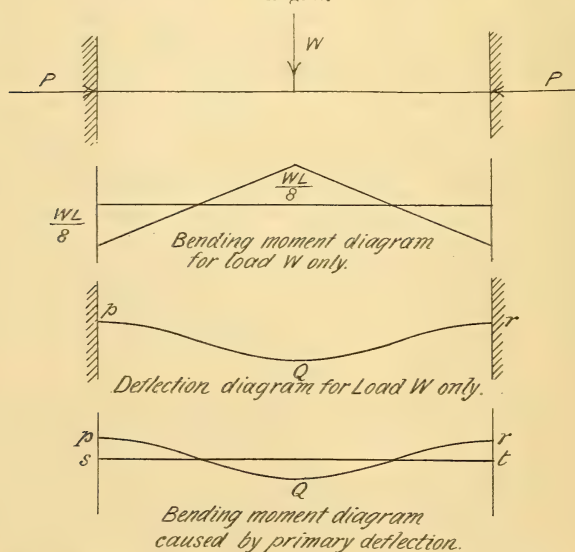


diagrams should be subtracted from the lateral load bending moment diagram, but otherwise the process remains exactly as before.

*Encastre and Continuous Beams.*—The method may be applied to the solution of encastre and continuous beams. The curve, however, into which the beam bends under both lateral and endlong loads does not, as in the case of free-ended or discontinuous beams, accurately represent the shape of the bending moment diagram for the end load. The fixing moments at the supports alter the base-line from which moments must be measured, and in general result in diminishing the moments due to the primary deflexion diagram. It is therefore even less necessary to consider the secondary deflexion effects than was the case with the free-ended beam.

Consider the case of the encastre beam under a regular system of loads and with an endlong load  $P$  applied along the neutral axis. Since the tangents at the extremities of such a beam are horizontal and therefore parallel to one another, the total area of the bending moment diagram between these two points must be zero, and this condition must apply to all bending moment diagrams drawn,

Fig. 2.

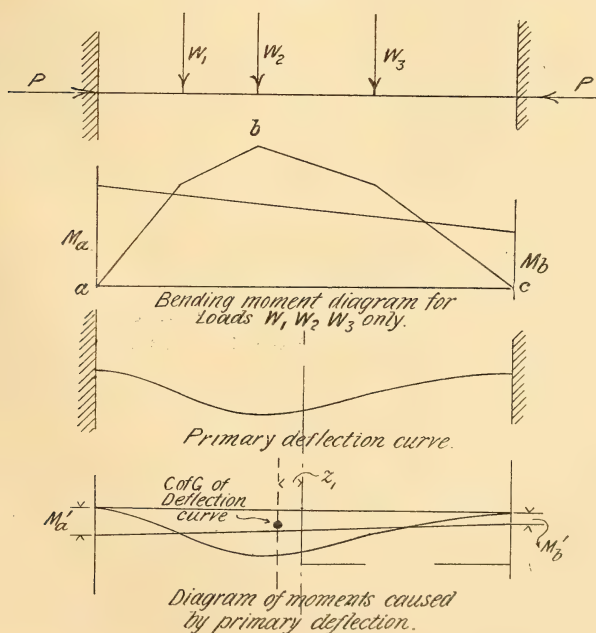


whether due to the lateral system only or to the diagrams obtained from the primary or secondary deflexion curves. Starting therefore from a bending moment diagram, fig. 2,

for the lateral loads only, it is necessary to draw the primary deflexion diagram  $pQr$ . A base-line  $st$  is then taken such that the area intercepted by the deflexion curve of the beam which lies above the base-line is equal to the area of that lying below the base-line. This diagram will then represent to scale the bending moments induced in the beam by the endlong load, supposing the beam to bend exactly to this shape. Should further accuracy be desired the secondary deflexion diagram may now be drawn and treated in a similar manner, that is, a base-line selected which shall make its total area equal to zero.

When a beam is under an irregular lateral load and is at the same time built in horizontally at the ends, an additional condition must be fulfilled by all the bending moment diagrams involved, whether due to the lateral system only or to the endlong loadings. This condition, which arises

Fig. 3.



from the fact that each support lies upon the tangent to the beam at the other abutment, states that the moment of the bending moment diagram about either end must be equal to zero. If  $abc$ , fig. 3, represents the curve of bending moments due to the lateral load acting upon the beam as a free-ended

girder, and if  $M_a$  and  $M_b$  represent the fixing moments at each end of the encastre beam, then

$$M_a = \frac{\Delta(c + 3z)}{2c^2}$$

$$M_b = \frac{\Delta(c - 3z)}{2c^2};$$

where

$c$  = the semi-span ;

$z$  = distance of centre of gravity of free-ended bending moment diagram from centre of beam ;

$\Delta$  = area of free-ended bending moment diagram ;

and the true bending moment diagram is obtained by setting up a base-line which is at a distance  $M_a$  above the base-line for the free-ended bending moment diagram at one end, and a distance  $M_b$  above at the other. If  $\Delta_1$  be now taken as the area of the deflexion curve and  $z_1$  to be the distance of the centre of gravity of the primary deflexion curve from the centre of the span, the true base-line from which the moments exerted by the endlong load should be measured is obtained by setting up ordinates at each end of the span equal to  $M_a'$  and  $M_b'$  where  $M_a'$  and  $M_b'$  are obtained from the above formula.

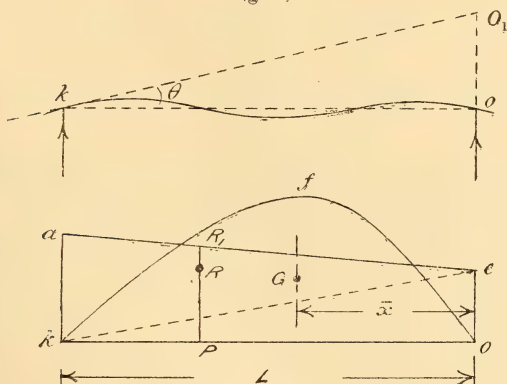
*Beam with Lateral Loading and End Load continuous over several supports.*—An important case of continuous beams with end loadings occurs in the case of aeroplane spars, particularly of the monoplane class where a light wood or metal spar is attached at one extremity to the fuselage of the machine and braced at intervals along its length by wires attached to the chassis.

Before the application of the method to beams of this type can be properly considered, it is necessary to consider shortly the means by which the bending moment diagram of continuous beams for lateral loads only may be drawn. The most convenient of the several methods of effecting the same purpose is that due to Claxton Fidler \*, who makes use of what he has called the “characteristic points” of the bending moment diagram.

\* For a full account of this method so far as it affects the solution of beams continuous over several supports and loaded in any manner but without end loading, the reader is referred to ‘Bridge Construction,’ by Claxton Fidler, chapter ix.

Let  $ko$ , fig. 4, represent any one span of a continuous beam loaded in any manner, and  $kfo$  be the bending moment diagram for the span taken as if it were discontinuous. Find

Fig. 4,



the area and position of the centre of gravity of  $kfo$ . Let the former be represented by  $\Delta$  and the distance of the latter from the right-hand support be taken as  $\bar{x}$ . Then we shall have

$$OO_1 = \theta L,$$

where  $\theta$  is the angle of slope of the beam at the left-hand support and  $OO_1$  is the distance by which the right hand support lies beneath the tangent to the left-hand support.

Now  $(OO_1)EI = \text{Moment of area of bending moment diagram about } o$ .

$$\begin{aligned} \therefore (OO_1)EI &= \Delta \bar{x} - (ak) \frac{2L^2}{6} - (co) \frac{L^2}{6} \\ &= \theta LEI. \end{aligned}$$

This can be written

$$EI \times 2 \frac{\theta}{L} = 2 \frac{\Delta \bar{x}}{L^2} - 2 \frac{(ak)}{3} - 2 \frac{(co)}{6}.$$

Now at a point P one third of the span from  $k$ , erect a perpendicular PR and make PR equal in length to  $\frac{2\Delta \bar{x}}{L^2}$ .

We have then

$$EI \times 2 \frac{\theta}{L} = PR - \left\{ \frac{2(ak)}{3} + \frac{2(co)}{6} \right\}.$$



But if  $R_1$  be the point where PR cuts the base-line  $ac$  we have :—

$$PR_1 = \frac{2}{3}(ak) + \frac{1}{3}(co)$$

$$\therefore EI \frac{2\theta}{L} = PR - PR_1 = -RR_1,$$

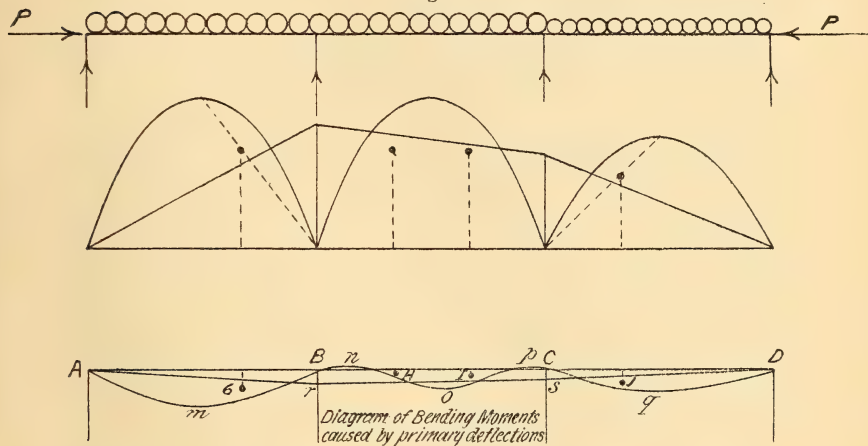
$$\text{or} \quad EI\theta = -\frac{RR_1 L}{2}.$$

In other words, the length  $RR_1$  when multiplied by the span of the beam is proportional to the slope of the beam at the support  $k$ . The same reasoning may be applied to the span lying to the left of  $k$ , and we shall get another point which is such that the distance by which the base-line passes over or under it, when multiplied by  $L$  is proportional to the slope of the beam over the support. Since if the slope of the beam is positive when proceeding from left to right it will be negative when proceeding from right to left, it follows that if the spans be equal the base-line must pass over the characteristic point on one side of the support and under the characteristic point on the other side of the support by equal distances. If the spans be unequal these distances will be inversely as the two spans. In order then to draw the complete bending moment diagram for a continuous beam, it is necessary firstly to draw the diagram for each span as though it were discontinuous. Secondly to find the position of each pair of characteristic points for each support and then complete the figure by drawing a broken line such that it passes over and under the characteristic points at each side of each support by equal distance or by distances inversely proportional to the spans. For uniform loads the method is very simple in application since the heights of the characteristic points above the free-ended base-line are equal to two-thirds the maximum height of the parabolic bending moment diagram for the span to which they belong.

Consider now the same beam having a load equal to  $P$  applied axially at each end. The bending moment diagram for the beam under the lateral load only may be drawn, and hence the curve of the bended beam under this loading only be obtained. This curve will not, as in the case of a discontinuous beam, exactly represent the bending moments due to the end load even supposing the beam to bend exactly to this shape. In order to obtain a diagram of bending moment due to the end loading it will be necessary to take

into account the moments at the supports which are caused by the bending of the beams. These moments are analogous to those obtained in the ordinary bending moment diagram for continuous beams, and will depend upon the shape of curve between the supports, *e. g.*, let *AmnopqD*, fig. 5,

Fig. 5.



represent the deflexion curve for the beam continuous over two supports and carrying loads of equal intensity over the two left-hand spans, and another uniform load of a different intensity over the right-hand span. Referring to the left-hand span, *AmB* would be the bending moment diagram for a beam of shape *AmB* under an end load if the beam were discontinuous over the support *B*. Since this is not the case and since a moment exists over the support *B*, the base-line for the curve of bending moments will be *Ar*. Similarly *rs* and *sD* will represent the bases for the centre and right-hand spans respectively. The arguments used in the proof of Claxton Fidler's method of drawing the ordinary bending moment diagrams for continuous beams apply equally well to this case, and it follows that if characteristic points *GHIJ* be drawn for the intermediate supports, the base-line must pass over and under the points on either side by equal amounts if the spans are equal, or by amounts inversely proportional to the two spans on each side of the support if the spans be unequal. This base-line being drawn we now know the bending moments induced in the beam by its being under end-long loading and being bent to the curve given by the primary deflexion diagram. Should further accuracy be desirable the secondary deflexion diagram may be drawn

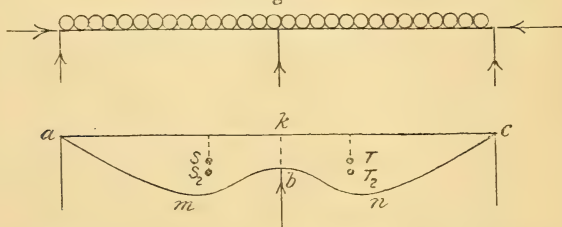
from this, and its base-line when considered as a bending moment diagram obtained exactly as before.

*Effect of Non-Alignment of Supports.*—It is a well known fact that in a continuous beam with lateral loads only a small amount of settlement or movement in any support may make a considerable modification in the magnitudes of the bending moments existing in the girder. It does not always follow that a movement in any one support will have large effects, but it is necessary to investigate the matter closely. The importance of this cannot well be overstated when designing continuous beams with end loads, since if the moments caused by the deflexion of the beam are sufficiently great to be taken into account, it is extremely likely that a comparatively slight movement in any support will be commensurate with the natural deflexion of the beam, and hence its effect in altering the moments due to the end load is considerable.

Referring again to a continuous beam with lateral loading only and assuming that a certain pier is out of line by an amount  $\delta$ , it is necessary first to find the characteristic points on the supposition that the piers are in alignment.

Set off to the scale of moments, distances equal to  $2EI \frac{\delta}{L_1^2}$  and  $2EI \frac{\delta}{L_2^2}$  above or below the original characteristic points according as the moment over the support is increased or decreased by the non-alignment of the pier. The points thus determined are the new characteristic points for the pier *c*. Since if any one support has settled by an amount  $\delta$ , it follows that in the case of a bridge of equal spans the supports to the right and left of the sunken pier will be left with a superelevation of  $\frac{\delta}{2}$  above the chord line, so that it is necessary in addition to alter the characteristic points for

Fig. 6.



these piers by an amount proportional to  $\frac{\delta}{2}$ , after which the base-line may be drawn exactly as before:

This method again may be applied to the beam with end loading, thus *ambnc* (fig. 6) is the primary deflexion diagram for a beam of two spans under a uniform load, in which the centre span has sunk by an amount  $\delta$ . Find the characteristic points  $S_2, T_2$ , at each side of the support  $b$ , carefully bearing in mind that area *akbm* is the one to be used in the expression for the distance of the characteristic point from the base-line *ac*. Next modify these characteristic points in accordance with the formulæ already considered in reference to continuous beams under lateral loading only.

*Conclusion.*—It will be seen that the method of successive graphical approximation is applicable to beams under end-long and lateral loading either continuous or discontinuous. The end load may or may not pass through the centre of the beam section. For large columns under practical conditions it is usually unnecessary to take into account the moments due to lateral deflexion, but under special circumstances of slender columns these moments may become of importance. For a simple system of loading on a beam of one span only the analytical method of solution presents many advantages, but if the lateral loading is complicated by the presence of unsymmetrical concentrated loads or by distributed loads of varying intensity, the graphical method is shorter and easily applied. For an analysis of a beam or tie continuous over several supports and subjected to end-long loadings it is, although long and complicated, the only method available.

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*XXI. The Effect of Ionization of Air on Electrical Oscillations, and its bearing on Long-Distance Wireless Telegraphy\*:*

*By Prof. G. W. O. HOWE, Imperial College, South Kensington †.*

WHILE it is true that Dr. Eccles' theory of the refraction of electromagnetic waves in the upper atmosphere is based on the assumption that ionization makes the atmosphere conducting, it must not be overlooked that this conductivity must, as Dr. Eccles has shown, be of a different type to that of ordinary materials, if it is to account for the observed phenomena. When a charged ion of molecular mass is situated in an alternating electric field

\* See Paper with this title by Prof. Barton and Mr. Kilby, *Phil. Mag.* Oct. 1913, p. 567.

† Communicated by the Author.



it is subjected to an alternating force, which causes it to oscillate about a mean position. If it is entirely free from frictional restraint, the acceleration in any direction will be a maximum when the force and therefore the field is a maximum in that direction. The molecule must have its maximum displacement in the opposite direction at this moment, and the electric current due to its motion will therefore lag  $90^\circ$  behind the electric field. This current is therefore in exact opposition to the pure displacement current, and has the effect of reducing the apparent dielectric constant of the medium. The velocity of propagation of electromagnetic waves should therefore be increased.

If the molecular motion is not free from frictional restraint, the current will not be in exact quadrature but will have a power-component, the relative magnitudes of the two components being dependent, among other things, on the freedom of molecular motion, that is, on the vacuum.

This phenomenon must not be confused with the comparatively well-known peculiarities of leaky condensers, *i. e.*, condensers shunted with a non-inductive resistance. Here the leakage current is in phase with the electric force, and therefore in quadrature with the displacement current. If  $R$ ,  $L$ ,  $C$ , and  $\frac{1}{S}$  represent the resistance, inductance, capacity, and shunt resistance of an oscillatory circuit, we have

$$f = \frac{1}{2\pi} \sqrt{\frac{1}{LC} - \left(\frac{R}{2L} - \frac{S}{2C}\right)^2}.$$

As the leakance  $S$  is increased from zero it counteracts the effect of  $R$  in decreasing the natural frequency, until, when  $S = \frac{RC}{L}$ , the frequency reaches a maximum. Further increase in  $S$  causes the frequency to decrease. This has no connexion, however, with the type of conductivity considered above.

*Ordinary leakage cannot increase the velocity of propagation of electromagnetic waves.*

This is readily seen from the formula for the velocity of propagation along a telephone line, which is

$$v = \frac{\omega}{q},$$

where  $\omega = 2\pi f$

and  $2q^2 = \sqrt{(R^2 + \omega^2 L^2)(S^2 + \omega^2 C^2)} - RS + \omega^2 CL,$

where the symbols refer to the values for unit length of the line. If  $R=0$ , this reduces to

$$\frac{2}{v^2} = LC \left( \sqrt{1 + \frac{S^2}{\omega^2 C^2}} + 1 \right),$$

from which it is seen that any increase in the leakage  $S$  causes a decrease in the velocity.

Now the results published by Prof. Barton and Mr. Kilby show agreement with the ordinary theory of the leaky condenser, and therefore indicate that the condenser with a dielectric of ionized air at atmospheric pressure had that type of conductivity or leakage which cannot cause an increase in the velocity of propagation, but can only cause a decrease of velocity and a certain amount of dissipative absorption.

The statement that "the work yields some experimental support to the theory of Dr. Eccles" appears therefore to be unjustified.

It would appear necessary to repeat the experiments with various vacua in the vessel containing the air condenser before the results could have any bearing on the theory put forward by Dr. Eccles.

XXII. *The Existence of Uranium Y.*  
By FREDERICK SODDY, M.A., F.R.S.\*

[Plate II.]

G. N. ANTONOFF (Phil. Mag. 1913 [6] xxvi. p. 1058) states that he has been able to repeat his experiments, which led him two years ago to conclude that a new product, uranium Y, of half-period 1·5 days, existed in the uranium series, with some purified uranyl nitrate obtained from me, and with which A. Fleck in this laboratory (Phil. Mag. 1913 [6] xxv. p. 710) was unable to obtain the same effects. I have pleasure in being able to confirm Antonoff's main result of an abnormal decay of the soft  $\beta$ -rays of uranium X, also with some of the same material. I approached the subject from a point of view which it seemed might account for the discrepancy between the two experimenters. It appeared possible that Antonoff's uranium Y might be isotopic † with uranium X, and that *any* chemical operation

\* Communicated by the Author.

† The terms "*isotopic elements*" or "*isotopes*" are convenient to indicate elements occupying the same place in the periodic table and therefore chemically indistinguishable and non-separable. See 'Nature,' December 4th, 1913, p. 400.

separating uranium X would separate uranium Y to the same extent. On this view, the obtaining of the effects would not depend on the use of any special chemical method, as Antonoff supposed, nor upon the use of a large quantity of uranium to give sufficient of the new product, supposed to be present in very small quantity, to be detected, but simply on the time of accumulation of the products since their previous complete separation. The proportion between uranium Y and uranium X would be a function only of this time of accumulation and would be the greater the shorter this time was made. This view is entirely at variance with what one would conclude from a perusal of Antonoff's original paper. Antonoff very kindly sent me privately further details of his chemical methods of separation, which confirmed my impression that it might be the time of accumulation rather than the method of separation which was of importance. My own experiments, so far as they go, have borne this out. I have not tried his particular method, but have got his result always when the time of accumulation of the uranium X was short, even when the uranium X was separated by barium sulphate, which he states gives uranium X free from uranium Y. It is therefore not altogether surprising that Fleck, who was unaware of the one condition necessary to obtain the effect in question, was not successful in repeating the work.

The main interest of Antonoff's discovery, as he himself points out, is that uranium Y might be the first member of the actinium branch series. Hahn and Meitner have suggested recently (*Physikal. Zeitsch.* 1913, xiv. p. 752) that uranium  $X_1$  may disintegrate dually, in both cases with expulsion of  $\beta$ -rays, producing therefore two isotopic "ekataantalums" in group VA, one the short-lived uranium  $X_2$  of Fajans and Göhring, and the other a still unknown long-lived parent of actinium in an  $\alpha$ -ray change, as I had suggested before uranium  $X_2$  was discovered. But if this possibility of a dual disintegration, the same kind of ray being expelled in both branches, is admitted, many alternatives can be framed. Thus, if either uranium I. or II. disintegrated dually in two  $\alpha$ -ray changes, the three products, uranium  $X_1$ , ionium, and the new branch product would be isotopic. The third product might be Antonoff's uranium Y, which then would be chemically non-separable from uranium  $X_1$ .

On such a view, since the period of uranium  $X_1$  is some twenty-four times that of uranium Y, and 8 per cent. of uranium atoms are supposed to follow the branch series, the

initial slope of the soft  $\beta$ -ray recovery curve of purified uranium should be considerably greater than that calculated for uranium X, for initially some two uranium Y atoms will be disintegrating for one of uranium X. Unfortunately the  $\alpha$ -rays of uranium are not much inferior in penetrating power to the soft  $\beta$ -radiation. Under conditions such that the  $\alpha$ -radiation of uranium is completely absorbed, the unabsorbed soft  $\beta$ -radiation produces only some 10 per cent. of the ionization produced by the hard  $\beta$ -rays. This makes the point very difficult to establish.

The apparatus used in the present work was designed from the value of the absorption coefficient in aluminium,  $300 \text{ (cm.)}^{-1}$ , given by Antonoff for the  $\beta$ -rays of uranium Y. After the experiments had been carried out a discrepancy was discovered, for from the curve given (Phil. Mag. 1911 [6] xxii. p. 427) this radiation is shown to be completely absorbed in aluminium equivalent to 4 cm. of air, and the absorption coefficient calculated from the curve is about three times greater than  $300 \text{ (cm.)}^{-1}$ . In my apparatus a total air equivalent of 4.7 cm. at  $15^\circ$  intervened between the preparations and the electroscope, but in spite of this discrepancy Antonoff's decay curves were clearly reproduced with the apparatus.

The preparations to be measured were spread uniformly on to the surface of circular ground-glass plates 17.7 cm. diameter,  $246 \text{ cm.}^2$  area, by moistening them with water and working them over the surface with a second very small ground-glass plate. The films were dried in the oven and the weight of material on them found by difference. The films of uranium oxide weighed usually 1.5 to 2 grams, or from 6 to 8 mg. per  $\text{cm.}^2$ , except in one case where only 0.3 g. was used. A specially wide and shallow electroscope, 19 cm.  $\times$  10 cm., was provided with a base of "grease-proof" paper covered with aluminium leaf, weighing  $5.27 \text{ mg. per cm.}^2$ , and equivalent in stopping power to 4.3 cm. of air at  $15^\circ$ . The surface of the preparations was placed 4 mm. below the paper base. The paper base and air-layer between the preparations and the electroscope were thus equivalent to 4.7 cm. of air, and would reduce the intensity of a radiation, for which  $\mu(\text{Al}) = 300 \text{ (cm.)}^{-1}$  to 0.525, and for which  $\mu(\text{Al}) = 500 \text{ (cm.)}^{-1}$  to 0.34 of the initial value. As screen, a sheet of celluloid weighing  $20.85 \text{ mg. per cm.}^2$  was used. This cuts down the hard  $\beta$ -rays of uranium X to 0.87, the soft  $\beta$ -rays with  $\mu(\text{Al}) = 300 \text{ (cm.)}^{-1}$  to 0.10, and those with  $\mu(\text{Al}) = 500 \text{ (cm.)}^{-1}$  to 0.02. Sometimes a thicker screen of aluminium, weighing  $73 \text{ mg. per cm.}^2$  was employed, instead of the celluloid.



Two series of experiments were performed, the first with 100 grams of the thorium-contaminated uranyl nitrate and the second with 50 g. of the purest uranyl nitrate, both as used by Fleck. Only the latter series need be considered in detail here. The method was to dissolve the crystals in ether in a tap-funnel, separating the aqueous layer, and washing a few times, each time with a few drops of water. The first aqueous extract containing the uranium X was rejected. The uranium was left to itself for periods varying from 20 hours to 4 days and the washing with a few drops of water then repeated, the uranium X being separated, from the aqueous layer of uranium solution obtained, by addition of a trace of ferric chloride, pouring into warm N/2 ammonium carbonate in the usual way, digesting a few minutes on the water bath and filtering through an ashless filter, which was ignited and spread over the ground-glass plate as described. From the ethereal solution, after settling, a few c.c. were siphoned off from the top into a platinum crucible, and ignited at once to oxide,  $U_3O_8$ , and spread over another plate. In all, the decay curves of five uranium X preparations and the recovery curves of five uranium oxide preparations were measured. The last uranium X preparation from the purest uranium was prepared by the barium sulphate instead of by the ferric method. The whole ethereal solution of uranium, after complete removal of uranium X, was ignited to uranium oxide. This weighed 15.25 grams and was dissolved in dilute nitric acid, the solution, almost neutralised with ammonia, being left to reaccumulate uranium X for 23 hours. Excess of sulphuric acid and a dilute barium nitrate solution was then added and the precipitated barium sulphate, weighing 89 milligrams, was got on to a glass plate in the usual way, as a film weighing about 0.35 mg. per cm.<sup>2</sup> All of the five uranium X preparations showed decay curves similar to those described by Antonoff, so that probably the reason why Antonoff did not observe the initial decay for uranium X separated by barium sulphate, is to be ascribed to some secondary cause, such as absorption in the material itself. For the barium sulphate and ferric oxide films, in which about one day had elapsed from the previous separation, the curves showed that about 30 per cent. of the total initial radiation was due to soft  $\beta$ -rays of the rapidly decaying radiation (fig. 1, Pl. II.). In those for which the time of accumulation was four days the proportion was about 16 per cent. The decay of the hard  $\beta$ -radiation was normal (Curves A II., A III., B II.). The decay of the total radiation was abnormal (Curves A I., B I.).

The difference curves (A IV., B IV.), obtained by extrapolating the observed curve for the total radiation, after the decay had become normal, back to the origin and subtracting this extrapolated curve, were roughly exponential. The half-value periods for different curves and for different parts of the same curve varied somewhat widely, between 20 and 33 hours, but was, as a mean, nearer 24 hours than 36 hours. Naturally, since one is dealing with only a 16 to 30 per cent. difference between an exponential and extrapolated curve, a considerable variation may be made in the individual values of the half-period, according to the way the points are chosen. Curves A IV. and B IV. were obtained from actual large scale pencilled curves and not from the necessarily rougher ink diagrams used for fig. 1. The results were corrected in terms of the hard  $\beta$ -rays of a standard preparation of uranium oxide, but it is clear that barometric and temperature changes must exert a considerable effect on the soft  $\beta$ -radiation which it is not easy to correct for. This probably accounts for the difficulty of getting the curves for the uncovered preparation as regular as those for the covered. Fig. 1 shows the decay curves for two preparations of uranium X separated from the purest uranyl nitrate, after a time of re-accumulation (A) of 19 hours by the ferric method, (B) of 23 hours by the barium sulphate method. The ordinates for the latter preparation have been doubled.

With regard to the recovery curves, there was some slight evidence of an initial slope greater than the theoretical. The smoothest and most regular curves, obtained from the purest uranium preparations, are shown in fig. 2 A. Curves A I. and A II. represent the curves for this preparation, bare and covered with the celluloid screen respectively. Curve A III. was obtained by subtracting from A I. a curve derived from A II. by increasing the ordinates by the factor 1.15 to allow for the absorption of the hard  $\beta$ -rays in the celluloid. This factor was determined experimentally, and the result agreed with that calculated from the absorption coefficient. It will be seen that A III. shows a distinct though small increase of slope over the first 100 hours during which uranium Y, if it exists as a separate product isotopic with uranium X, would be attaining the equilibrium value. This increase of slope, though hardly beyond the region of experimental error, is of the right order to be expected from the curves fig. 1.

Taking the A curves of fig. 1, the time of accumulation was 19 hours. If the period of uranium Y is 1.5 days, 0.41 of the equilibrium amount would be present and the

equilibrium value of the "extra" radiation due to uranium Y (Curve A IV.) would be about 14 d.p.m. The radiation due to 19 hours accumulation of uranium X is 22 d.p.m., so that in equilibrium this radiation will be about 1000 d.p.m. The ratio is 1.4 per cent. From Curve A III. (fig. 2) it follows that the equilibrium "extra" radiation due to the uranium Y is 1.6 d.p.m., whereas that due to the uranium X would be about 100 d.p.m., in substantial agreement with the former result.

The soft  $\beta$ -radiation of the uranium X in the A curves (fig. 1) is about 3 d.p.m., corresponding with 136 d.p.m. in equilibrium. The ratio of this to the 14 d.p.m. contributed by the uranium Y is again of the order to be expected if the latter is the parent of actinium in a branch claiming 8 per cent. of the total atoms disintegrating, and if each atom of uranium X and uranium Y gives, on disintegration, a similar amount of ionization. The same result can also be deduced from the recovery curves. The equilibrium soft  $\beta$ -radiation of a film of uranium oxide such as was employed in the A curves, fig. 2, is about 12 d.p.m.

The uranium oxide in this experiment (fig. 2, curves A) weighed 1.96 g. or 8 mg. per cm.<sup>2</sup> In the hope of obtaining clearer evidence of the increased initial slope of the recovery curve, the curves were taken for another uranium oxide preparation weighing only 0.3 g. or 1.2 mg. per cm.<sup>2</sup>. It is shown in fig. 2, curves B I. and II. The hard  $\beta$ -radiation is thus reduced 6 or 7 times. The total radiation, however, was so exceedingly small that though the curves were taken with the utmost care, several hours being spent on each set of measurements, the variations of the individual points from the smoothed curve are too great to allow of the difference curve being drawn with any certainty. But here also it can be shown that a much more marked difference of slope than that of A III., fig. 2, is not to be expected. For even in the thicker film, weighing 8 mg. per cm.<sup>2</sup>, more than 50 per cent. of a radiation, for which  $\mu(\text{Al}) = 300 \text{ (cm.)}^{-1}$ , would escape absorption, so that for an infinitely thin film the relative initial increase of slope could not be so great as twice that shown in A III. (fig. 1). On the whole I am inclined to believe that the recovery curves do show a real but very small effect due to uranium Y, which is not much beyond the possible error of measurement. Clearly it will be very difficult to get more conclusive evidence on this point.

Finally, a search was made for  $\alpha$ -radiation by the method formerly used (Phil. Mag. 1909 [6] xviii. p. 859), the preparation being mounted on a rectangular slip of metal placed between the poles of a powerful electromagnet in an

electroscope filled with hydrogen, measurements being taken in the magnetic field with the preparation alternately bare and covered with a mica strip. In the former work, with large quantities of uranium, a quickly decaying  $\alpha$ -radiation would not have been detected. In the present experiments, only 200 grams of the purest uranyl nitrate were employed, and the uranium X was separated from it, as described, with as little loss of time as possible. In one experiment only 30 minutes elapsed between the end of the separation and the first measurement. Measurements were continued for several days, but no evidence of a rapidly decaying  $\alpha$ -radiation was observed. The actual  $\alpha$ -ray leak amounted to less than a division a minute and remained sensibly constant. It may well have been due to a trace of uranium.

If uranium Y is the parent of actinium it is to be expected, since it appears to be isotopic with uranium X<sub>1</sub>, that one  $\alpha$ - and one  $\beta$ -particle must be expelled from it before actinium is produced. So far, there is no evidence of the  $\alpha$ -ray change.

#### *Summary.*

(1) Antonoff's main result regarding the abnormal decay of the soft  $\beta$ -rays of uranium X has been confirmed, but the abnormal decay was obtained for all uranium X preparations, however separated, for which the time of reaccumulation was short.

(2) If uranium Y has a separate existence it appears to be isotopic with uranium X<sub>1</sub>. This makes it unusually difficult to obtain further evidence as to whether it has a separate existence.

(3) The recovery curves of the  $\beta$ -rays of uranium after separation of uranium X reveal some slight evidence of the existence of uranium Y, which though scarcely beyond the limit of possible error is shown to be of the right order to be expected.

(4) The ionization contributed by uranium Y is about of the order to be expected if it is the parent of actinium in a branch claiming 8 per cent. of the atoms, and if the atoms of uranium X<sub>1</sub> and Y produce equal ionizations on disintegration.

(5) No evidence was obtained of an  $\alpha$ -radiation from uranium X + Y separated as rapidly as possible from uranium.

I desire to acknowledge the assistance rendered by Mrs. Soddy, who carried out most of the large number of measurements involved in the work.

Physical Chemistry Laboratory,  
Glasgow University.  
Dec. 10, 1913.



XXIII. *Notices respecting New Books.*

*Researches of the Department of Terrestrial Magnetism. Land Magnetic Observations 1905-1910.* By L. A. BAUER, Director of the Department. (Quarto; pp. 185.) Washington, 1912.

THE Department of Terrestrial Magnetism of the Carnegie Institution of Washington came into existence in April 1904, and has for one of its principal objects the acquisition of the data necessary for a general magnetic survey of the Earth. This volume deals with all the land observations made by the Department up to the end of 1910. It gives a general account with illustrations of the types of instruments used, describes the methods of taking and reducing observations, and enumerates in tabular form the values obtained for the magnetic elements at 1298 stations scattered over the globe. The continents chiefly represented are Africa with 386 stations, North America with 328, and Asia with 308. The observers—including some foreigners employed on special expeditions—numbered 35. Descriptions are given intended to fix the exact site of each station, and a number of interesting photographs collected in plates show representative sites in different parts of the world.

*Practical Measurements in Radio-activity.* By W. MAKOWER, M.A., B.Sc., and H. GEIGER, Ph.D. Pp. ix + 151. Longmans, Green & Co. 1912. Price 5s. net.

THE well-known researches of both the authors of this book are sufficient to inspire confidence in the reader even before he reads the book itself, and the confidence is not misplaced. The authors have a first-hand acquaintance with the subject and, besides this, one of them at least has a large experience as a teacher. The result is a book which is a complete compendium of the science of radioactivity from the point of view of practical measurements, with enough of the theory thrown in to make the volume self-contained. On the physical side perhaps the most important chapter is that on standard measurements, while the final chapter deals with the various methods, both chemical and other, of separating radioactive substances. Three appendices contain tables of radioactive constants, tables of decay of radioactive substances, and notes on radioactive materials and measuring instruments.

XXIV. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. xxvi. p. 548.]

November 5th, 1913.—Dr. Aubrey Strahan, F.R.S., President ;  
in the Chair.

THE following communication was read :—

‘Geological Sections through the Andes of Peru and Bolivia.’

By James Archibald Douglas, M.A., B.Sc., F.G.S.

This paper deals with the geological structure of the South American Andes, as illustrated by a horizontal section drawn from the port of Arica in the extreme north of Chile (formerly Peruvian territory) across the mountain-ranges or ‘Cordilleras’ to the forested region of the Amazon slopes, in the district known as the Bolivian ‘Yungas,’ following the route of the new Arica-La Paz railway, which was under course of construction at the time of the author’s visit.

It is the partial result of two years’ geological exploration in Peru, undertaken on behalf of Mr. W. E. Balston, F.G.S., for the Oxford University Museum. After a description of the general physiography of the Peruvian Andes, the topographical features of the country traversed by the railway are discussed in some detail.

Its geological structure is then described under three headings:—

- (1) The Mesozoic sediments of the coastal region with their contemporaneous igneous rocks, the intruded core of granodiorite, and the overlying recent volcanic rocks of the Western Cordillera.
- (2) The volcanic rocks of the Mauri River, the Mesozoic and Palæozoic sediments of the ‘Altaplanicie’ and the Titicaca district; the line of dioritic intrusions, and the Pleistocene gravels of the Desaguadero River.
- (3) The Palæozoic rocks and granitic core of the Eastern Cordillera and the Amazon slopes.

(1) The Mesozoic stratified rocks are well exposed in the ‘Morro de Arica,’ where fossils occur which indicate an Upper Jurassic (Callovian) age. They are interbedded with thick sheets of basic enstatite-andesite, showing well marked ‘pillow’-structure; this rock is remarkably fresh, and free from albitization.

Similar stratified rocks are traced up the Llutah and Palca river-valleys. In the former they are penetrated by a thick intrusion of quartz-hypersthene-norite, which, it is suggested, is the plutonic equivalent of the pillow-lava of the coast.

The erosion of the river-valleys that has brought to light the Jurassic sediments has also laid bare the underlying plutonic mass of granodiorite, which may be regarded as the deep-seated core of the Western ‘Cordillera.’ This plutonic mass appears to have been intruded in the form of a batholite in post-Cretaceous times.

The Western Cordillera is essentially a volcanic range, formed of numerous more or less isolated, snow-capped, dormant and extinct volcanoes, attaining heights of 19,000 to 20,000 feet. The

enormous amount of volcanic material emitted from these cones has almost completely concealed the underlying rocks.

The lavas can be resolved into three main groups, characterized by their dominant ferromagnesian mineral, succeeding one another in age according to a law of increasing basicity:—

- (i) Acid rhyolites and tuffs with biotite.
- (ii) Trachytes and trachy-andesites with hornblende, typically developed in the district of Mount Taapaca.
- (iii) Andesites and basalts with pyroxenes, forming the cones of Mounts Tacora and Chupiquiña.

(2) The western part of the high-level Bolivian plateau, or 'Altaplanicie,' is almost entirely covered by vast horizontal sheets of volcanic ash, tuff, and pumiceous lava, described as the Mauri Volcanic Series. These rocks have often the appearance of 'trass,' and it is suggested that they have been formed in large part as subaqueous deposits. The occurrence in an interbedded layer of gravel, of a fragment of a jaw of '*Nesodon*,' almost identical in appearance with specimens from the Miocene beds of Santa Cruz, affords the only clue for an estimation of their age. They are overlain on the east by gravel-deposits of the Desaguadero River, the highest terrace of which was found to contain remains of *Mastodon*, *Megatherium*, *Scelidotherium*, and other Pleistocene vertebrates.

From beneath these superficial deposits crops out a series of unfossiliferous red and chocolate-coloured sandstones and conglomerates. After comparison with other districts on the north, these are divided into two groups—a younger gypsiferous sandstone and marl series of Cretaceous age, broken through by a line of dioritic intrusions and resting with pseudoconformity on an older Permo-Carboniferous group. The latter ends abruptly along a fault-line against vertical shales and quartzites, containing a few characteristic Lower Devonian fossils. These Devonian beds, though much concealed by alluvial plains, form the basement of the eastern part of the 'Altaplanicie.'

The Carboniferous formation is nowhere exposed along the line of section; but an account is given of its development in the region of Lake Titicaca, where the limestones contain an Upper Carboniferous or Permo-Carboniferous marine fauna.

A short discussion is entered into on the theory of the recent elevation of the Andes and the origin of Lake Titicaca.

(3) The Eastern Cordillera rises to heights of over 22,000 feet, being composed chiefly of steeply-dipping Devonian slates and quartzites, though many of the unfossiliferous black slates and greywackés of the eastern slopes most probably may be referred to the Silurian, or even to an older formation. Outcrops of granite are of rare occurrence along the line of section, although there is reason to suppose that this rock forms the core of most of the high peaks. As marine Lower Carboniferous and Upper Devonian rocks are absent from this district, it is suggested that the granitic core was intruded during a period of land-elevation at this time.

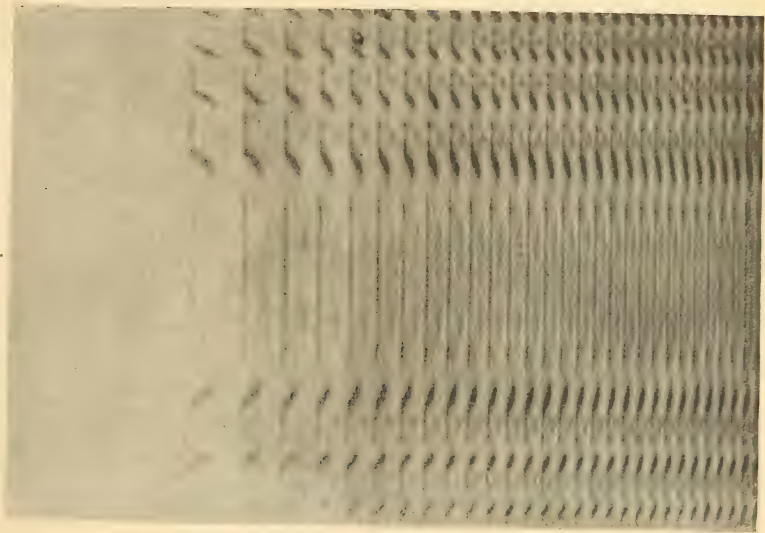


# Crossed Spectra.

Fig. 2.

5461

L.G. Plate  
combined  
with F.P. Plate.



4359

Echelon combined with L.G. Plate.

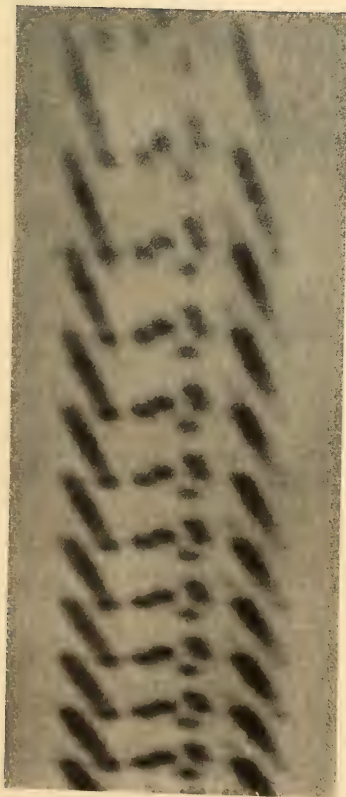


Fig. 1.

Echelon combined with F.P. Plate.

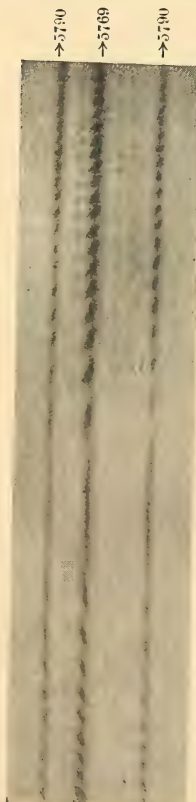


Fig. 4.



Fig. 3.



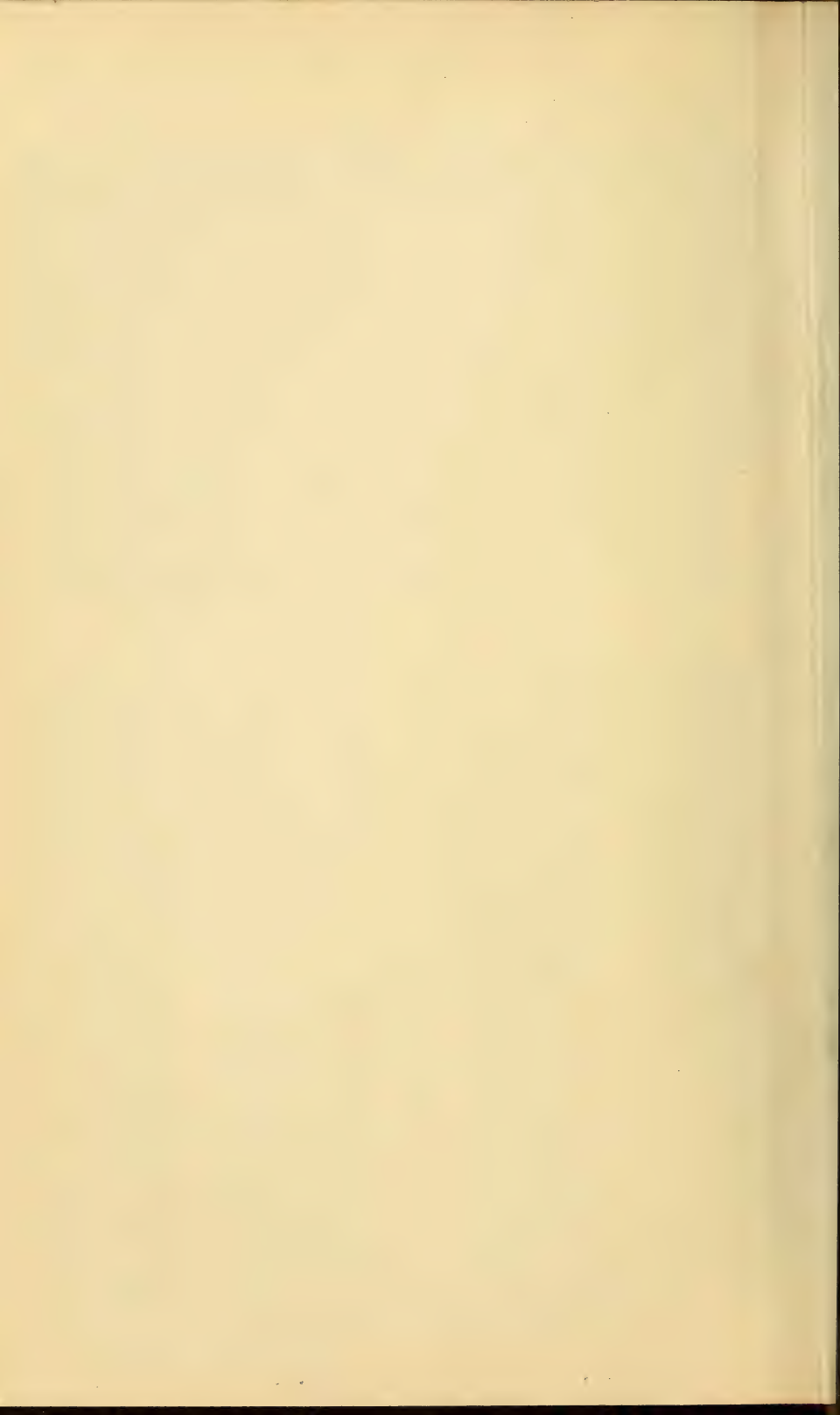
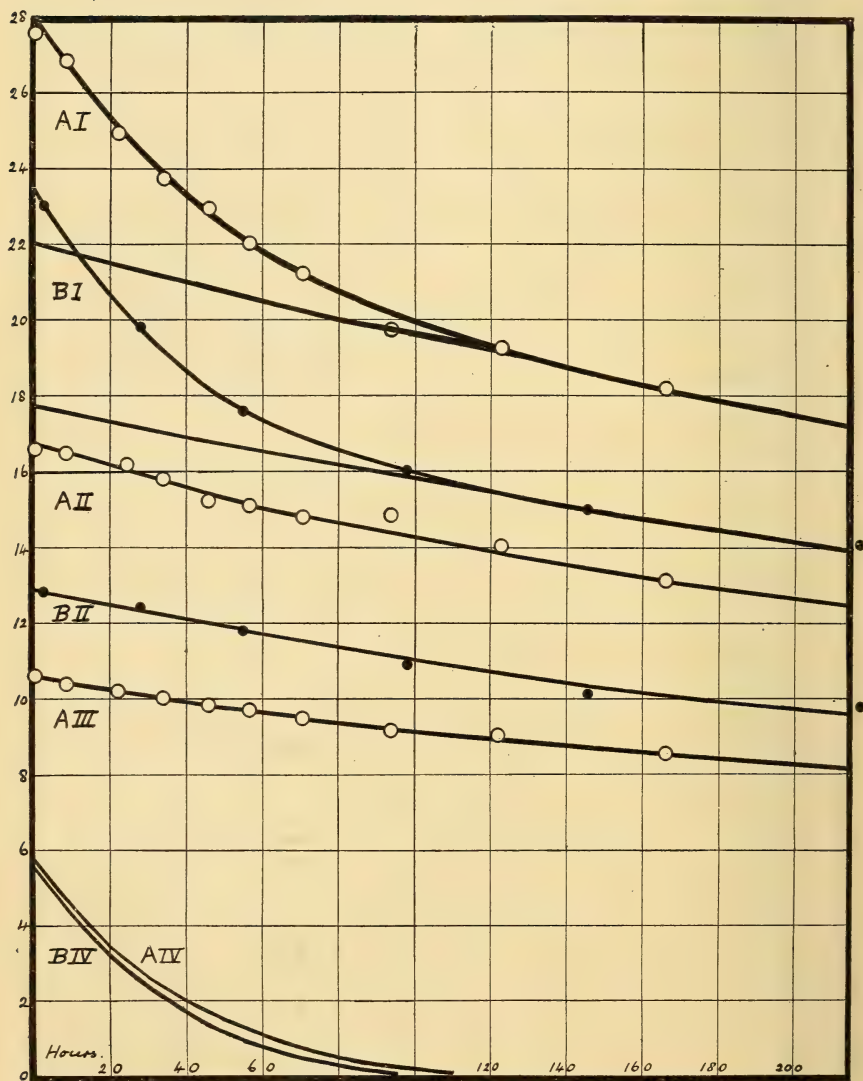




FIG. 1.



DECAY CURVES OF URANIUM X.

A. Uranium X separated by ferric method after 19 hours accumulation.

B. Uranium X separated by barium sulphate after 23 hours accumulation.

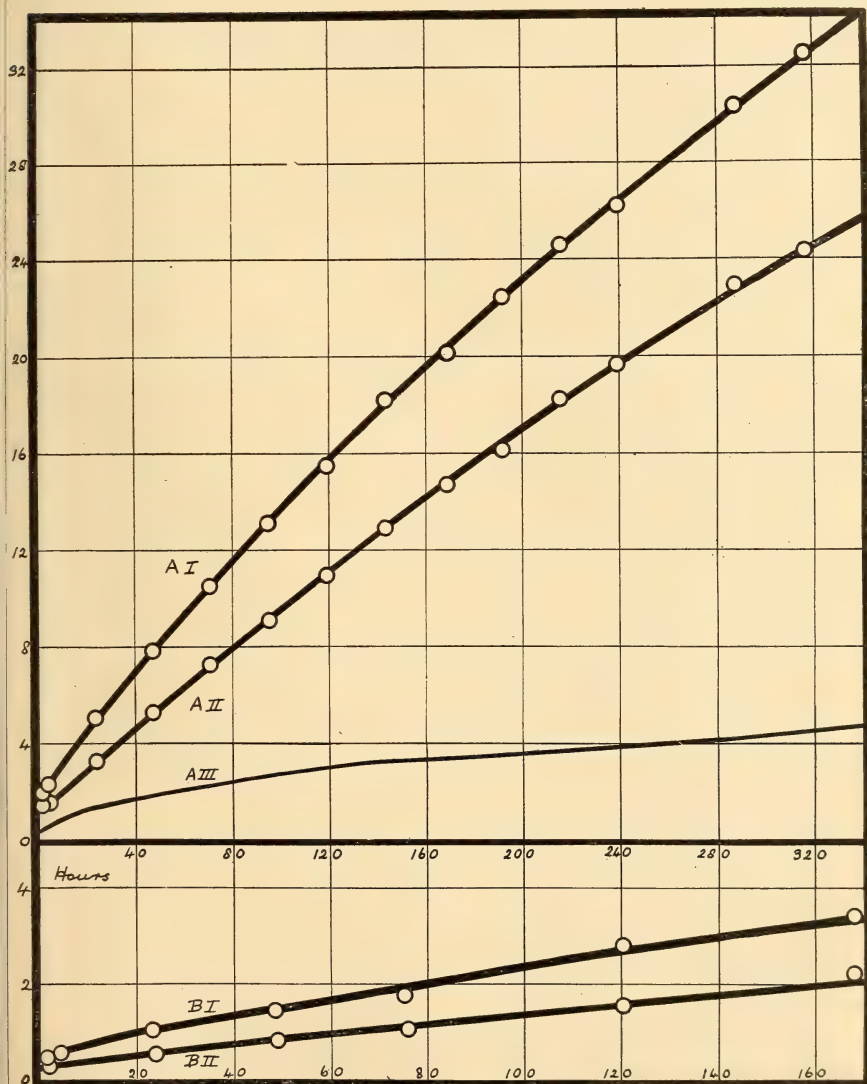
A I., B I., preparation bare.

A II., B II., preparation covered with celluloid screen.

A III., preparation covered with aluminium screen.

A IV., B IV. Difference curves by subtracting the extrapolated curve from A I. and B I.

FIG. 2.



RECOVERY CURVES OF URANIUM OXIDE.

A. Weight of film 1.96 grams or 8 mg. per cm.<sup>2</sup>

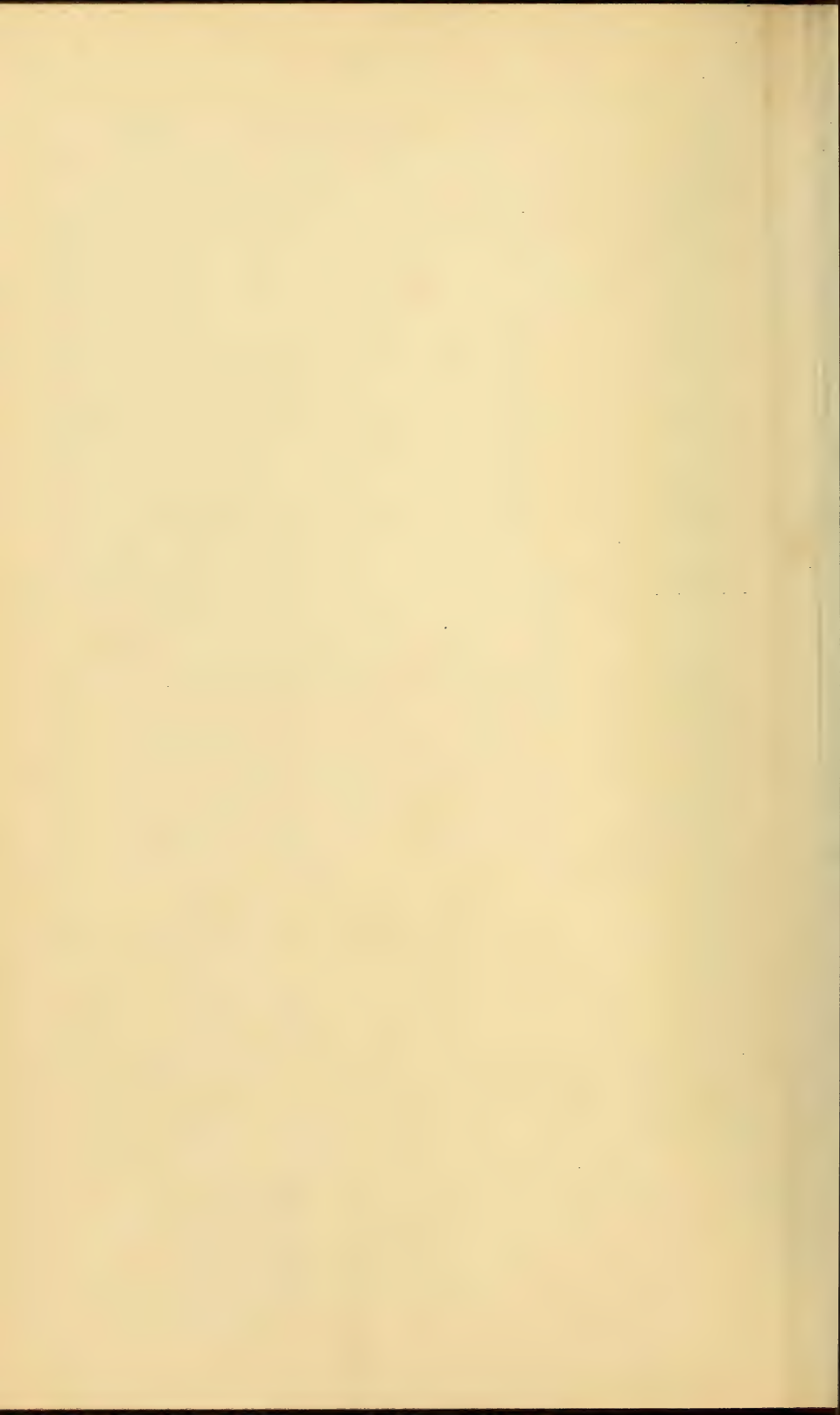
B. Weight of film 0.3 gram or 1.2 mg. per cm.<sup>2</sup>

A I., B I., preparation bare.

A II., B II., preparation covered with celluloid screen.

A III. Difference curve by subtracting from A I. the curve A II. with the ordinates increased by the factor 1.15.





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AND  
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

FEBRUARY 1914

XXV. *Secondary  $\gamma$  Radiation.* By D. C. H. FLORANCE,  
M.A., M.Sc., Assistant Lecturer and Demonstrator, Uni-  
versity of Manchester\*.

THERE has been considerable discussion during the past few years regarding the homogeneity of the  $\gamma$  rays emitted by radium C. As a result of an investigation by Mr. and Mrs. Soddy and Mr. Russell† it was concluded that the  $\gamma$  rays of radium were initially homogeneous, and that the absorption of the  $\gamma$  rays was strictly exponential up to a thickness of 22 cm. of lead. It was not known till after their experiments that radium B emitted some  $\gamma$  rays whose penetrating power is considerably less than those emitted by radium C. It is clear, therefore, that the  $\gamma$  rays emitted by radium were initially complex.

Rutherford and Richardson‡ have shown that the  $\gamma$  rays of radium B consist of three types which are exponentially absorbed in aluminium with absorption coefficients  $230 \text{ cm.}^{-1}$  and  $40 \text{ cm.}^{-1}$  and  $0.51 \text{ cm.}^{-1}$  respectively, while the  $\gamma$  rays from radium C consist essentially of one type which are also exponentially absorbed in aluminium with an absorption coefficient  $0.115 \text{ cm.}^{-1}$ . Rutherford§ has, moreover, put forward the view that the  $\gamma$  rays of radium C

\* Communicated by Prof. E. Rutherford, F.R.S.

† Mr. & Mrs. Soddy and Mr. Russell, *Phil. Mag.* May 1910.

‡ Rutherford & Richardson, *Phil. Mag.* May 1913.

§ Rutherford, *Phil. Mag.* October 1912.

are characteristic of that element and correspond to the "characteristic radiation" of the K series established by Barkla. These characteristic radiations are absorbed according to an exponential law and have generally been considered to be homogeneous. Recent experiments\* on the reflexion of X rays from the surface of crystals have made it clear that these characteristic radiations may consist of several types of radiation of definite wave-lengths and with definite absorption coefficients in aluminium. For the present we may assume that the  $\gamma$  rays emitted from radium C are initially homogeneous; but the experiments described in this paper show conclusively that  $\gamma$  rays cease to be strictly homogeneous after passing through matter. In fact there is a continuous transformation taking place throughout the whole range of absorbing screens.

In the following experiments a tube filled with radium emanation served as a source of  $\gamma$  rays. The tube was first surrounded with lead 0.084 cm. thick, so that the two soft types of  $\gamma$  rays from radium B were completely absorbed, and the emergent  $\gamma$  rays were due chiefly to the  $\gamma$  rays of radium C and to a certain extent to the  $\gamma$  rays of radium B, whose absorption coefficient in aluminium was  $0.51 \text{ cm.}^{-1}$ . Then a screen of lead 1.14 cm. thick was added, which is sufficient to absorb almost completely the  $\gamma$  rays from radium B. The penetrating radiation which emerges consists of unchanged  $\gamma$  rays from radium C, together with a radiation that has been in some manner transformed in passing through the absorbing screen. However much additional material the rays pass through there is always present with the primary radiation a transformed radiation indicating that there is a continuous change in type of the primary beam in each successive absorbing screen. The emergent radiation is always complex; but since the loss of energy in any layer is always proportional to the energy entering that layer, the  $\gamma$  rays of radium C have been described as being "homogeneous." But it must be understood that the term "homogeneous" in this case has a different meaning from that applied to the  $\gamma$  radiation from radium C which has not passed through absorbing screens. It is probable in the latter case that the radiation initially does not contain that distribution of softer types of radiation which are always present after the  $\gamma$  rays have passed through matter. It was shown by Soddy (*loc. cit.*) that the  $\gamma$  rays of radium were exponentially absorbed by lead,

\* W. H. & W. L. Bragg, Proc. Roy. Soc. July 1913. Moseley & Darwin, Phil. Mag. July 1913.

whether the whole beam was used as in the case of the hemispherical absorbers, or whether part of the beam was used as in the ordinary absorption experiments. Hence since this transformed radiation is always present, it is evident that an exponential law of absorption cannot be regarded as a definite proof that the emergent radiation is homogeneous, *i. e.*, unchanged in type in passing through matter. At the same time the exponential law of absorption for the  $\gamma$  rays of radium C indicates that part of the  $\gamma$  radiation persists unchanged in type after passing through great thicknesses of matter. Some of the radiation is always being transformed into softer types of radiation in passing through matter; but equilibrium is soon set up between the primary and the transformed radiation, so that the combined primary and secondary radiations are absorbed according to an exponential law.

The following experiments were carried out to see if any evidence could be adduced to explain how a primary radiation like the  $\gamma$  radiation from radium C, consisting essentially of one type, gives rise to a very complex secondary radiation. In the case of X rays we know that characteristic radiations are produced under suitable conditions, and that scattering of the primary rays also takes place. Gray\* showed that the  $\gamma$  rays of radium E produced in certain elements radiations characteristic of them. The writer†, in his earlier experiments, was unable to detect any characteristic radiation excited by  $\gamma$  rays of radium C, and concluded that all the materials examined simply scattered the primary  $\gamma$  rays. But in those experiments the side of the electroscope was 3 mm. of lead, so that any absorbable type of radiation would not have been detected in the electroscope.

In re-investigating this question it was necessary to bear in mind that since the  $\gamma$  rays of radium C are characteristic of that element, it might be anticipated from the analogy of X rays that these  $\gamma$  rays should excite characteristic radiation in elements of high atomic weight and should be scattered by elements of low atomic weight.

For the sake of convenience the secondary radiation is divided into two parts, the "emergent," *i. e.*, the radiation emitted from the radiator in the direction of the primary radiation, and the "returned," *i. e.*, the radiation emitted from the incident surface of the radiator. There is no essential difference in these two radiations, except that the returned radiation is less penetrating than the emergent.

\* Gray, Proc. Roy. Soc. September 1912.

† Florance, Phil. Mag. December 1910.



In the paper an investigation has been made on the following questions :—

1. The quality of the secondary radiation or its variation in penetrating power with
  - (a) position of electroscope;
  - (b) position of radiator;
  - (c) material of radiator;
  - (d) screening of emanation.
2. The absorption of the primary beam and its consequent effect on the secondary radiation.
3. The distribution of secondary radiation depending on
  - (a) thickness of radiator;
  - (b) material of radiator;
  - (c) equal masses of different radiators ;
  - (d) material of the side of the electroscope;
  - (e) screening of the emanation;
  - (f) use of air or methyl iodide in the electroscope.
4. The energy of the scattered radiation.
5. Evidence of a characteristic radiation and reason for assuming that the secondary  $\gamma$  radiation is a modification of the primary radiation.

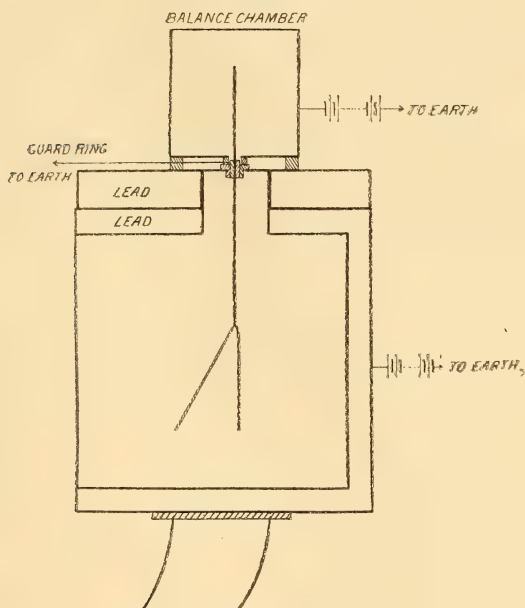
#### *Experimental Arrangement.*

A diagrammatic sketch of the electroscope and experimental arrangement is given in fig. 1 and fig. 2. The direct ionization effect could be reduced to any extent by a suitable adjustment of lead screens and by a balance method. As far as possible screens were chiefly employed, since with a large direct effect combined with a very active source on the balance-chamber, the results were uncertain and it appeared that under these conditions the sulphur insulation became conducting. The secondary radiation was examined in four positions of the electroscope which are denoted by the symbols  $E_1$ ,  $E_2$ ,  $E_3$ ,  $E_4$ . The electroscope was 12 cm. cube externally and the sides were of lead 1 cm. thick, except the front face which was either of aluminium .202 cm. thick or of lead .084 cm. thick. The radiators were all 11 cm. square. The distance between the centre of rotation and the front face of the electroscope was approximately 25 cm.

The emanation could be screened by lead of any definite thickness. The secondary radiation could be absorbed

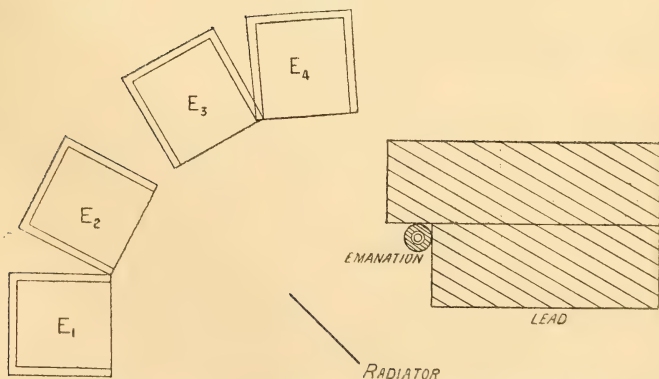
directly by placing the absorber against the electroscope or indirectly by placing the absorber in front of the emanation.

Fig. 1.



Electroscope and Balance-chamber

Fig. 2.



Experimental arrangement for the examination of the secondary  $\gamma$  radiation.

I. *The Quality of the Secondary Radiation.*

The radiator was so placed that its centre approximately coincided with the centre of rotation of the electroscope. The side of the electroscope through which the rays entered was an aluminium plate .202 cm. thick. The quality or penetrating power of the secondary radiation was measured by placing a lead screen .084 cm. against the aluminium side of the electroscope and also by adding a second lead plate .303 cm. thick. In Table I. are given these absorption coefficients in lead for the four positions of the electroscope. The emanation was screened with lead .084 cm. thick, so that the primary rays consisted of a mixture of  $\gamma$  rays from radium B and from radium C.

TABLE I.

Radiator.	Absorption coefficients in lead.							
	$E_1$ . Angle $43^\circ$ .		$E_2$ . Angle $70^\circ$ .		$E_3$ . Angle $103^\circ$ .		$E_4$ . Angle $127^\circ$ .	
	.084 cm.	.303 cm.	.084 cm.	.303 cm.	.084 cm.	.303 cm.	.084 cm.	.303 cm.
1.06 cm. zinc.	2.70	1.75	4.20	2.6	6.5	4.8	10.6	5.2
0.63 cm. lead.	...	...	2.5	1.7	9.2	3.0	11.4	3.6

The emanation was then screened with lead 1 cm. thick so that the  $\gamma$  rays from radium B were no longer present. The absorption coefficients are measured in .084 cm. of lead and the results are tabulated in Table II.

TABLE II.

Radiator.	Absorption coefficients measured in .084 cm. lead.			
	$E_1$ .	$E_2$ .	$E_3$ .	$E_4$ .
1.06 cm. zinc.....	1.5	3.4	5.5	7.5
0.63 cm. lead .....	.96	2.2	5.5	9.9

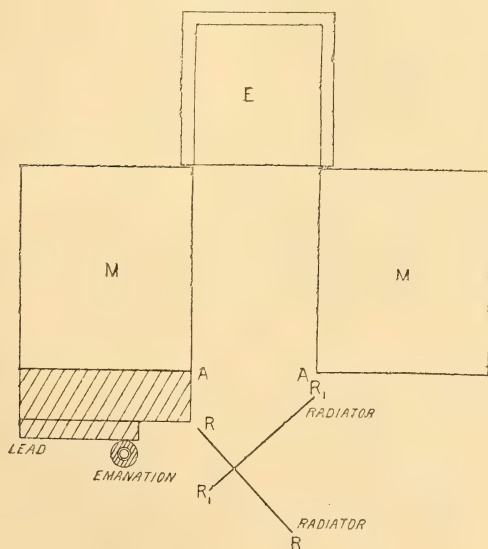
These values confirm and extend the results already obtained by the writer, that the penetrating power of the

secondary radiation depends on the direction in which the radiation emerges from the radiator, on screening the emanation, and to a certain extent on the material of the radiator ; and that the secondary radiation for any definite direction is not homogeneous. Recent experiments with zinc as the radiator placed at different angles, show that the absorbability of the secondary radiation depends largely on the direction in which it is issuing and not altogether on the fact of its being "emergent" or "returned."

Examining the absorption coefficients included in the tables, it is seen that the emergent secondary radiation from lead is more penetrating than from zinc, but the "returned" radiation from lead is less penetrating at least for the first screen. It appears then that from lead there arises a type of radiation less penetrating than that from zinc and probably characteristic of lead.

This point had previously been investigated with radiators of lead, mercury, and platinum. The experimental arrangement is shown in fig. 3.

Fig. 3.



MM is a large electromagnet giving a field strength about 1400 gauss when the pole-pieces are 9 cm. apart. The side of the electroscope consists of mica equivalent to about 6 cm. of air. The absorbing screens are placed at AA and the radiators in the positions R<sub>1</sub>R<sub>1</sub> and RR. The electroscope



was airtight, so that methyl iodide could be introduced when necessary.

The general conclusions drawn from a large number of experiments are these: When elements such as aluminium, carbon, and iron are used as radiators, there is no evidence of the presence of a very easily absorbed radiation. The "returned" radiation has an absorption coefficient of  $\cdot 20 \text{ cm.}^{-1}$  to  $\cdot 30 \text{ cm.}^{-1}$  in aluminium compared with  $\cdot 115$  for the direct radiation. Aluminium is not so effective in absorbing the secondary radiation as lead, and in consequence is not so suitable for measuring the quality of the radiation.

On the other hand, in the case of the elements lead, platinum, and mercury, there is always an indication of the presence of a soft type of radiation, especially noticeable in the "returned" radiation. This appeared most marked in the case of platinum, but it was difficult to prove conclusively since nothing better than a platinum dish was available for a radiator. The absorption coefficients of the returned radiation in aluminium varied between  $\cdot 50 \text{ cm.}^{-1}$  and  $\cdot 80 \text{ cm.}^{-1}$  for the first 3 or 4 mm. of absorbing material.

Additional experiments have been made using a thin sheet of lead about  $0\cdot 01 \text{ cm.}$  thick and  $15 \text{ cm.}$  square as a radiator. The returned radiation could be detected with certainty through lead  $0\cdot 084 \text{ cm.}$  thick. With an absorbing screen of lead  $0\cdot 01 \text{ cm.}$  thick the absorption coefficient was found to be about  $40 \text{ cm.}^{-1}$ . Accurate readings were impossible on account of the smallness of the radiation observed. The absorption coefficient in  $0\cdot 202 \text{ cm.}$  of aluminium was found to be about  $1\cdot 5 \text{ cm.}^{-1}$ . In these experiments a mixture of hydrogen and methyl iodide had been introduced into the electroscope. The absorption coefficients in successive thicknesses of lead absorbing-screens are included in the following table:—

Absorbing-screens of lead .....	$0\cdot 01 \text{ cm.}$	$0\cdot 02 \text{ cm.}$	$0\cdot 03 \text{ cm.}$	$0\cdot 04 \text{ cm.}$	$0\cdot 088 \text{ cm.}$
Absorption coeff- cient .....	40	32	24	20	13

While there is undoubtedly a very soft radiation present in the  $\gamma$  rays returned from lead, it is difficult to be certain whether this is to be ascribed to the excitation of one of the characteristic types of radiation from lead. At the same time there is no evidence to contradict such an assumption.

*Absorption of the Primary Radiation.*

In these experiments four radiators were employed consisting of carbon, aluminium, zinc, lead, each of weight about 470 grs. The ionization currents were measured in the electroscope when the radium emanation was screened with lead  $\cdot 084$  cm. thick and when it was screened with lead ( $\cdot 084 + 1\cdot 14$  cm.) thick. Allowing of course for the effect without the radiator in position, the absorption coefficient of the direct radiation was thus indirectly determined.

Table III. contains the results for the four positions (fig. 2) when the side of the electroscope was  $\cdot 202$  cm. aluminium.

TABLE III.

Radiator.	Absorption coefficients measured in $1\cdot 14$ cm. lead.			
	$E_1$ .	$E_2$ .	$E_3$ .	$E_4$ .
2.26 cm. carbon ...	$\cdot 88$	$\cdot 90$	$\cdot 90$	$\cdot 88$
1.3 cm. aluminium .	$\cdot 84$	$\cdot 90$	$\cdot 90$	$\cdot 88$
0.5 cm. zinc .....	$\cdot 85$	$\cdot 85$	$\cdot 85$	$\cdot 88$
0.326 cm. lead .....	$\cdot 70$	$\cdot 67$	$\cdot 87$	$\cdot 88$

From Table III. it is seen that when carbon, aluminium, and zinc are used as radiators, the distribution of the secondary radiation is independent of the "hardness" of the primary  $\gamma$  rays ; but this is not the case with lead as radiator, for now the lead absorbs the softer  $\gamma$  rays from radium B, which in the case of the other radiators would probably have appeared on the emergent side. Experimenters have generally found with X rays that the scattered rays are of the same penetrating power as the primary rays, so that a screen placed in the primary beam will absorb these rays in the same proportion as it would absorb the scattered radiation when placed in front of the electroscope. This is by no means true with the  $\gamma$  rays and the secondary  $\gamma$  rays. It would therefore appear that the secondary  $\gamma$  rays must be the outcome of a transformation in the primary beam. This question will be discussed later in the paper.

In Table IV. are given the corresponding results when the side of the electroscope was  $\cdot 084$  cm. lead.

TABLE IV.

Radiators.	Absorption coefficients measured in 1.14 cm. lead.			
	$E_1$ .	$E_2$ .	$E_3$ .	$E_4$ .
2.26 cm. carbon ...	.77	.77	.71	.74
1.3 cm. aluminium .	.77	.77	.72	.75
0.5 cm. zinc .....	.77	.73	.70	.71
0.326 cm. lead .....	.66	.61	.63	.64

The lead side of the electroscope has now cut off a considerable portion of the secondary radiation due to the  $\gamma$  rays of radium B, and in consequence the absorption of the primary beam has apparently been decreased. The lead screen reduces the emergent and the returned radiation in the same proportion for the lead radiator.

*The Distribution of Secondary Radiation  
round the Radiator.*

Some experiments were made to examine the distribution of secondary radiation under varying conditions.

The emanation was screened with lead 1 cm. thick and the side of the electroscope was an aluminium plate .202 cm.

In figs. 4, 5, 6, 7 are shown the relations between the secondary radiation and thickness of radiator for the four standard positions  $E_1$ ,  $E_2$ ,  $E_3$ ,  $E_4$  respectively of the electroscope. In the same figures the relations between the secondary radiations for equal weights of carbon, aluminium, zinc, and lead and their atomic weights are also given. None of these readings have been corrected for the absorption of the secondary radiation in the material of the radiator or for the absorption in the side of the electroscope.

These corrections are uncertain and, moreover, considering the difficulty of always reproducing exactly the same conditions, it has been useless for the present to aim at anything but general conclusions.

At first sight it would appear that substances of low atomic weight produce more secondary radiation than substances of high atomic weight. It is to be noticed from the figures that only with a thickness of lead less than 0.05 cm. is the secondary radiation as great as from the corresponding mass of zinc. Yet if a suitable correction be made for the absorption of the secondary radiation, it seems that lead produces

more secondary radiation than does a similar mass of zinc ; and this is in accordance with the results obtained for X rays.

Fig. 4.

The zinc radiators were increased in thickness from 0.5 cm. to 2.5 cm., and the lead radiators from 0.085 to 1.6 cm.

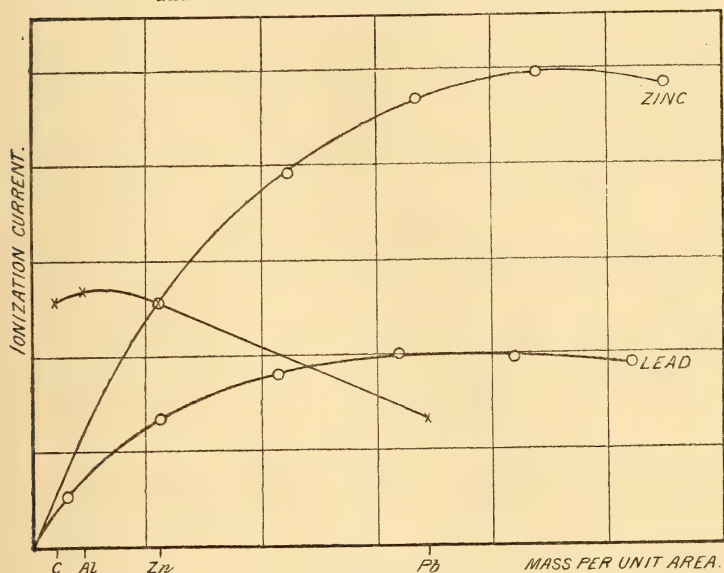


Fig. 5.

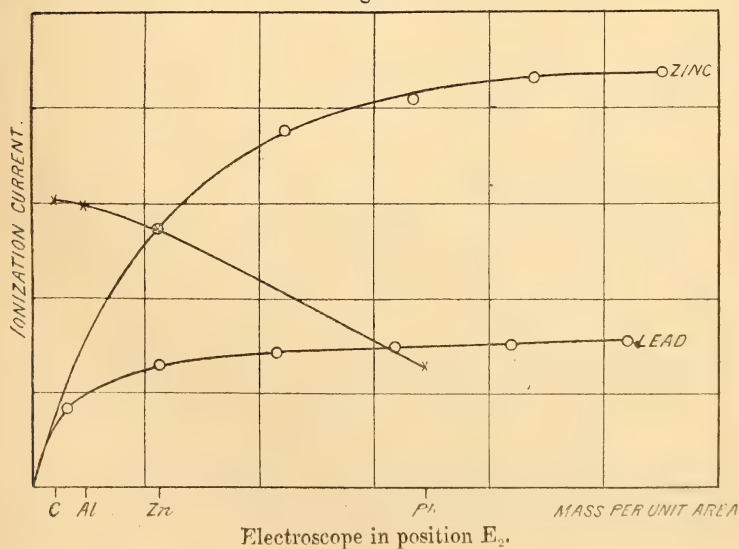




Fig. 6.

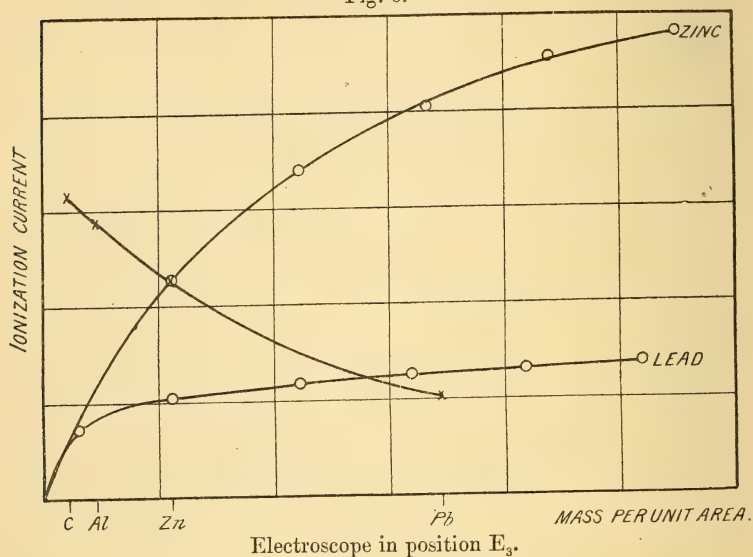
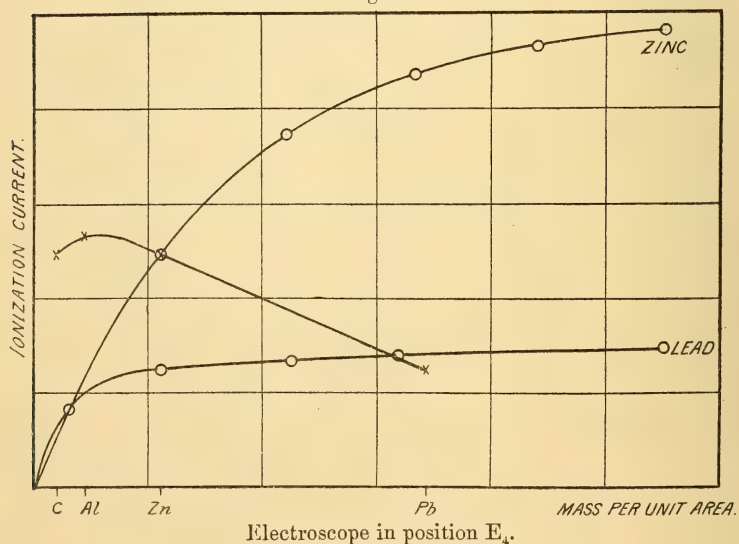


Fig. 7.



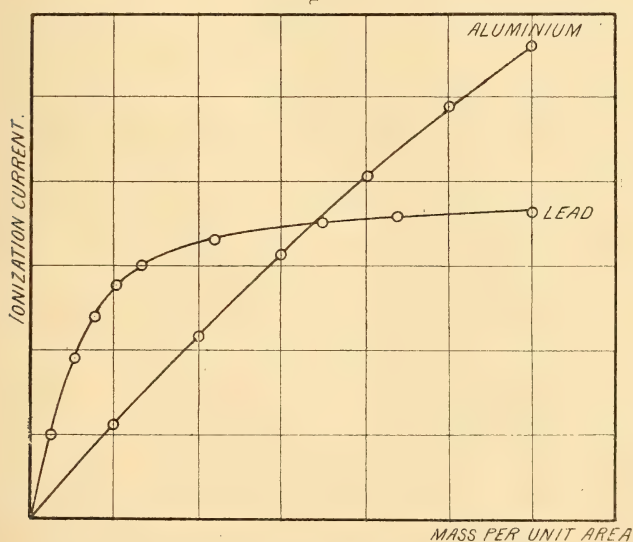
When equal weights (470 grs.) of the four radiators are used, carbon does not always produce more secondary radiation than aluminium. This had been observed in the earlier

experiments of the writer when the side of the electroscope was three millimetres of lead. When very penetrating X rays are allowed to impinge on carbon, Peeling\* has shown that carbon acts in an anomalous manner.

Similar curves were obtained when the emanation was surrounded by a screen of lead  $\cdot 084$  cm. thick.

In figure 8 are given the ionization currents when the lead radiator was increased in thickness from  $0\cdot 01$  cm. to about  $0\cdot 38$  cm., and when the aluminium radiator was increased from  $0\cdot 161$  cm. to  $0\cdot 96$  cm. The experimental arrangement was similar to that shown in fig. 3. It is clearly seen that lead produces more "returned" radiation than does an equal mass of aluminium.

Fig. 8.



The returned radiation when the lead radiators are increased in thickness from  $0\cdot 01$  cm. to  $0\cdot 38$  cm., and the aluminium radiators are increased from  $0\cdot 161$  cm. to  $0\cdot 96$  cm.

#### *Varying the side of the Electroscope.*

In the above experiments the side of the electroscope was always aluminium. It was thought that the side of the electroscope through which the rays enter might exercise a definite influence over the apparent distribution of the secondary radiation. It is well known that the relative amount of  $\beta$  rays produced in different materials is dependent

\* Peeling, Phil. Mag. Nov. 1912.

on the character of the  $\gamma$  radiation. A few experiments were therefore performed under the following conditions:—

- A. The side of the electroscope was lead .084 cm. thick.
- B. The side of the electroscope was aluminium .202 cm. thick.
- C. A combination of these two plates with lead inside.
- D. A combination of these two plates with aluminium inside.

In Table V. the values, in arbitrary units, of the ionization currents are given for equal weights of the four standard radiators when the radium was screened with .084 cm. of lead, and the conditions were those of A and B.

TABLE V.

Radiators.	E <sub>1</sub> .		E <sub>2</sub> .		E <sub>3</sub> .		E <sub>4</sub> .	
	Al.	Pb.	Al.	Pb.	Al.	Pb.	Al.	Pb.
2.26 cm. carbon .....	168	150	88	65	69	39	78	33
1.3 cm. aluminium ...	170	156	80	66	63	38	80	37
0.5 cm. zinc. ....	159	150	64	59	44	32	75	36
0.326 cm. lead .....	83	82	25	24	19	11	35	16

These numbers are only approximate but they illustrate the general distribution in these four positions of the electroscope.

The effect of the lead screen becomes more marked in the returned part of the secondary radiation. Although this was to be expected on account of the greater absorption of returned radiation, it was at the same time thought there should have been a corresponding increase in the production of emergent  $\beta$  rays from the lead. For instance, in case C, when there was a combination of the two plates and the lead was innermost, the distribution of secondary radiation was similar to that obtained when lead alone was used and allowance made for the absorption of the radiation in the aluminium plate. On the other hand, when aluminium was innermost, the distribution was again relatively similar to that obtained with lead alone, but with the values of the ionization currents about 20 per cent. less. It is therefore clear that more  $\beta$  rays are set free in the lead than in

aluminium, but sufficient experiments have not been made to show how far the quantity of  $\beta$  rays set free depends on the quality of the secondary radiation. This does not appear to be sufficiently marked to make it an effective method for distinguishing radiations. According to Bragg's results\*, tin and carbon would be the best materials to use for contrasting this production of  $\beta$  rays. A combination of two plates of tin and carbon has recently been tried. The ionization current is always slightly greater when tin is the inside plate. The contrast is not as marked as when a compound plate of aluminium and lead is used.

The emanation was then screened with another piece of lead 1.14 cm., and the distribution examined with aluminium and then lead as the side of the electroscope. The absorption coefficients in this lead screen have already been included in Tables III. and IV., and they illustrate the corresponding alteration in distribution.

Whatever radiator has been so far employed and whether the emanation was screened with lead .084 cm. thick or with lead (.084+1.14 cm. thick) there has always been a preponderance of the emergent over the returned radiation. This increases the nearer the electroscope is brought to the direct primary beam on the emergent side of the radiator.

First of all let us examine the returned radiation when the side of the electroscope consists of aluminium. The results obtained with a side of lead need not be considered, as a large correction is required for the absorption of the radiation in the plate. The distribution of the returned radiation from aluminium, zinc, and lead apparently corresponds to the distribution anticipated from the ordinary theory of scattering. There is always a greater proportion returned normally to the plate than at right angles to the primary beam.

On the other hand, carbon appears to be an exception. There is evidence of a greater scattering of the radiation at right angles to the primary beam when the proper corrections are made for absorption.

In the case of the emergent radiation the same peculiarities are observed as with X rays. There is a marked dissymetry in the returned and the emergent radiation and the quantity emerging in any given direction is dependent on the material of the radiators.

It is important in these experiments to know to what extent the ionization current depends on the penetrating power of the radiation examined. It would appear that the

\* Bragg and Madsen, *Phil. Mag.* December 1908.



energy given up by the secondary  $\gamma$  radiation is not strictly comparable with the energy given up by the primary  $\gamma$  rays. If this is the case then the distribution observed by means of an electroscope filled with air would not be a measure of the real distribution of the energy of the primary and secondary radiations. An experiment was carried out to determine the distribution of the secondary radiation when the electroscope contained a mixture of hydrogen and methyl iodide. The radiators used were .326 cm. lead and .5 cm. zinc, and the results are compared in Table VI. with those obtained when air was the gas in the electroscope.

TABLE VI.

Radiators.	E <sub>1</sub> .		E <sub>2</sub> .		E <sub>3</sub> .		E <sub>4</sub> .	
	Air.	Methyl iodide.	Air.	Methyl iodide.	Air.	Methyl iodide.	Air.	Methyl iodide.
0.326 cm. lead..	100	100	30	32	23	29	42	63
0.5 cm. zinc ...	192	190	77	78	53	57	90	100

The ionization current when the electroscope was in position E<sub>1</sub> and the radiator was lead, has been taken equal to 100. The side of the electroscope was .202 cm. aluminium. It is at once seen that the observed distribution depends largely on the gas within the electroscope. This is especially noticeable when lead is the radiator. This result supports the view that a softer radiation is produced in the lead, and this is most marked on the incident side of the plate. The values obtained for the absorption coefficients of the secondary radiation will also to a certain extent be dependent on the fact that the softer radiation gives up a greater proportion of its energy.

#### *The Energy of the Secondary Radiation.*

The range of distribution examined was of necessity limited, and therefore, to determine the total secondary radiation, a comparison was made with earlier experiments, and approximate values have been assigned in the unexplored parts of the field. The energy of the primary radiation falling on an aluminium radiator 1.3 cm. thick was calculated. Then an approximate estimation was made of the total secondary radiation by graphically integrating over

the whole sphere a small portion of which had been explored with the electroscope. It was thus found that 13 per cent. of the total energy of the primary beam falling on this radiator appeared as secondary radiation. A correction of course is necessary for the absorption of the secondary radiation in the material of the radiator. This correction factor would be of the order 1.5, so that the total secondary radiation would probably be not more than 20 per cent. of the primary beam.

Let us for the present assume this value, so that the total energy of the secondary radiation is 0.20 of the energy of the primary beam. Consequently, for a radiator of unit mass per square centimetre we have

$$\frac{\text{Energy in secondary radiation}}{\text{Energy in primary radiation}} = 0.05 \text{ approx.}$$

Comparing this with the value 0.20 found by Barkla\* it appears that aluminium scatters the  $\gamma$  rays to a much less extent than the X rays.

If this aluminium radiation had been used simply as an absorbing screen for  $\gamma$  rays from radium C, then not more than 20 per cent. of the rays would have disappeared from the primary beam. But it has been shown that this 20 per cent. absorption can be approximately accounted for by the production of secondary  $\gamma$  radiation. We have still to account for the energy of the  $\beta$  rays emitted during the passage of  $\gamma$  rays through matter. If, as is generally supposed, the  $\beta$  rays receive their energy from the  $\gamma$  rays, then in the above calculation we have overestimated the energy contained in the secondary  $\gamma$  radiation. From the results of experiments carried out with methyl iodide it is clear that these ionization experiments do not express accurately the intensity of the radiation in different directions; and before the distribution of the energy can be definitely determined it will be necessary to know what correction must be made for this greater liberation of energy the less penetrating the radiation becomes.

In all investigations on the secondary  $\gamma$  radiation it has been definitely shown that it is less penetrating than the primary radiation. The writer has shown that there is no sudden change in character from the primary to the secondary  $\gamma$  radiation. Consider first of all the case when aluminium or zinc is used as a radiator and the emanation tube is surrounded with lead 1 cm. thick. The penetrating power

\* Barkla, *Phil. Mag.* May 1904 & May 1911.

of the secondary radiation from the zinc measured in a screen of lead 0.084 cm. thick is given in Table II. It is seen that the secondary  $\gamma$  radiation is gradually changing in type and that the radiation becomes less penetrating the more its path is removed from the original direction of the primary beam. This secondary  $\gamma$  radiation is not only completely heterogeneous taken as a whole, but it is also heterogeneous when a limited region is examined. This heterogeneity is most marked when lead is used as the absorbing screen. For radiators such as aluminium and zinc characteristic radiations were not expected; and in these experiments there was no indication of such a radiation.

The general view at the present time regarding the scattered X rays is that they are of the same penetrating power as the primary X rays. Webster\* has put forward an explanation for the distribution of scattered X rays, and he points out that a diminution in the penetrating power of the radiation is to be expected. If the secondary  $\gamma$  radiation we have been examining is a result of scattering, then the scattering of  $\gamma$  rays must involve some modification in the primary  $\gamma$  rays. The early view that scattering consisted in the sifting out of the various components of the original primary beam is no longer tenable. This is obvious from the fact that after the primary beam has passed through 1 cm. of lead and then through a lead radiator 1 cm. thick, there is still present a soft secondary radiation which must have been completely absorbed had it been an untransformed constituent of the primary beam. In other words, the  $\gamma$  rays emerging from any thickness of material appear to possess the same power of producing secondary rays. A similar conclusion has been arrived at by Gray†.

We seem, therefore, to be reduced to two conclusions, that either these secondary  $\gamma$  rays are the primary rays scattered and in the course of scattering the rays have lost energy and have become altered in type, or a complete transformation has taken place and these radiations are true secondary radiations. This latter hypothesis is not supported by experimental evidence. The secondary radiation is not in any way characteristic of the material from which it emerges. The secondary  $\gamma$  rays do not appear therefore to be intimately connected with the atoms of the radiator apart from the fact that the atoms act as scattering centres. Moreover, although

\* Webster, Phil. Mag. February 1913.

† Gray, Phil. Mag. October 1913.

we know that  $\gamma$  rays in passing through matter give rise to  $\beta$  rays and that  $\beta$  rays excite  $\gamma$  rays, the amount of the transformed  $\gamma$  radiation is far greater than could be explained on this point of view.

It is necessary to adopt the first view, that the primary  $\gamma$  rays during the process of scattering lose energy and are in consequence modified in type. With a lead radiator, after the secondary  $\gamma$  radiation has passed through 0.084 cm. of lead, the radiation appears to be similar to that produced from an aluminium or zinc radiator.

In the case of radiators such as platinum, mercury, and lead, there is besides the ordinary type of secondary  $\gamma$  radiation an "extra radiation" of a more absorbable type. The amount of this radiation is small, but its effect can be considerably increased when methyl iodide is used in the electro-scope. This radiation is mainly detectable as a returned radiation from the incident surface of the radiator. Although a large number of experiments have been made it is impossible at present to say with certainty that this extra-radiation is a characteristic radiation of the radiator concerned. When platinum was used as a radiator this extra-radiation was more marked, and it appeared to be softer than that from mercury or lead. Another probable explanation is that the extra-radiation is due to  $\beta$  rays excited in the material of the plate; since the  $\beta$  rays rapidly lose energy in passing through matter, this might explain the presence of the small percentage of soft  $\gamma$  rays.

### *Summary.*

1. An investigation has been made on the emergent and returned secondary  $\gamma$  radiations, using radium emanation as a source of primary  $\gamma$  rays. The experiments confirm the author's earlier results that the secondary  $\gamma$  radiation becomes gradually less penetrating the greater the angle it makes with the original direction of the primary beam. The penetrating power depends to a certain extent on the thickness of the radiator and on the screening of the emanation. The secondary  $\gamma$  radiation is completely heterogeneous.
2. The secondary  $\gamma$  radiation for all radiators is different in type from the primary radiation, and it appears that in the process of scattering some modification has taken place.



3. In the case of elements such as platinum, mercury, and lead there is a small amount of an "extra-radiation" with an absorption coefficient of about  $40 \text{ cm.}^{-1}$  in lead. This "extra-radiation" may be characteristic of the radiator.
4. The production of secondary  $\gamma$  rays plays an important part in the absorption of the primary  $\gamma$  rays.
5. Lead produces more secondary  $\gamma$  rays than does an equal mass of aluminium, zinc, or tin.
6. The distribution of the secondary radiation has been examined under various conditions.

I wish to express my best thanks to Prof. Rutherford for the supply of large quantities of emanation and for his advice during the course of these experiments.

XXVI. *Some Electromagnetic Effects related to the Hall Effect.* By E. P. ADAMS, *Professor of Physics, Princeton University* \*.

A NUMBER of interesting electromagnetic effects were described by Professor Corbino two years ago (*Physikalische Zeitschrift*, xii. pp. 561, 842, 1911), which have an important bearing on the electron theory of metallic conduction. The theory of the experiments given by him does not lead directly to results which admit of numerical calculation. He introduces both positive and negative carriers of electricity, and his results involve the mobility of these two kinds of ions. It is the purpose of this paper to develop the theory of these effects in terms of the electrons and their characteristics. While it is certain that the simple electron theory of metallic conduction, involving collisions with the atoms like those between hard elastic spheres, is very imperfect, it seems worth while to examine its consequences in these cases. The results obtained are very simple and furnish an excellent opportunity of testing the hypotheses involved.

The three electromagnetic effects predicted and discovered by Professor Corbino are the following :—

(1) A metallic circular disk in which a uniform radial electric current flows is placed in a magnetic field at right angles to its plane. There results a circular current in the plane of the disk such that the current density is inversely proportional to the radius.

(2) The disk with the radial current flowing in it is

\* Communicated by the Author.

suspended in a magnetic field so that its normal is inclined to the lines of force. A torque is produced tending to turn the disk.

(3) A radial current is induced in the disk on exciting a magnetic field at right angles to its plane. An equal and opposite radial current is induced when the field is destroyed.

It is necessary to consider the motion of electrons in a circular disk when a radial current flows. Let  $C$  be the whole radial current,  $\tau$  the specific resistance of the metal,  $d$  the thickness of the disc,  $r_1$  and  $r_2$  its internal and external radii. The current must be thought of as entering the disk through a wire of radius  $r_1$  at its centre, and as leaving uniformly from all points of its periphery of radius  $r_2$ .

The radial force acting on an electron of charge  $e$  is

$$\frac{C\tau}{2\pi rd} = \frac{a}{r} \quad \text{where } a = \frac{C\tau}{2\pi d}$$

and there is no tangential force. The equations of motion of an electron are :

$$\frac{d^2r}{dt^2} - r\left(\frac{d\theta}{dt}\right)^2 = \frac{ae}{mr}, \quad . . . . . (1)$$

$$\frac{1}{r} \frac{d}{dt} \left( r^2 \frac{d\theta}{dt} \right) = 0, \quad . . . . . (2)$$

$m$  is the mass of the electron. (2) gives

$$r^2 \frac{d\theta}{dt} = k, \quad . . . . . (3)$$

and this with (1) gives

$$\frac{d^2r}{dt^2} = \frac{k^2}{r^3} + \frac{ae}{mr}.$$

Integrating :

$$\left(\frac{dr}{dt}\right)^2 = A - \frac{k^2}{r^2} + \frac{2ae}{m} \log r. \quad . . . . . (4)$$

The electrons are assumed to move equally in all directions with velocity  $v$  between collisions when there is no electric field. The effect of the electric field is to give them a drift in its direction. After a collision the electron begins to move with velocity  $v$  in a wholly random direction. During its free path, until its next collision, it is acted upon by the electric force; we must now find the average velocity it

acquires in this direction. Consider an electron which moves away from a collision at the point  $r' \theta'$ , in a direction making an angle  $\alpha$  with the radius. At the beginning of its free path its radial and tangential velocities are :

$$\frac{dr}{dt} = v \cos \alpha,$$

$$r \frac{d\theta}{dt} = v \sin \alpha.$$

From (3) the constant  $k$  is determined :

$$k = r' v \sin \alpha,$$

and using this in (4) the constant  $A$  is determined :

$$A = v^2 - \frac{2ae}{m} \log r'.$$

Therefore the radial velocity of the electron during its free path is given by

$$\left(\frac{dr}{dt}\right) = v^2 \cos^2 \alpha + \frac{2ae}{m} \log \frac{r}{r'}.$$

At the end of its free path the value of  $r$  will be approximately

$$r' + \lambda \cos \alpha,$$

where  $\lambda$  is the length of the free path of the electron. So its radial velocity at the end of its free path is given by :

$$\left(\frac{dr}{dt}\right)^2 = v^2 \cos^2 \alpha + \frac{2ae}{m} \log \left(1 + \frac{\lambda \cos \alpha}{r'}\right);$$

$\frac{\lambda \cos \alpha}{r'}$  is very small compared with unity. This may then be replaced by :

$$\left(\frac{dr}{dt}\right)^2 = v^2 \cos^2 \alpha + \frac{2ae\lambda \cos \alpha}{mr'}.$$

The average radial velocity acquired under the influence of the electric force is one-half the difference of its radial velocities at the end and beginning of its free path. This gives for the radial velocity during the free path :

$$\overline{\frac{dr}{dt}} = \frac{1}{2} v \cos \alpha \left\{ \left( 1 + \frac{2ae\lambda}{mv^2 r' \cos \alpha} \right)^{\frac{1}{2}} - 1 \right\}.$$

As the second term in the parentheses is very small compared with unity, this reduces to

$$\frac{dr}{dt} = \frac{ae\lambda}{2mvr} \dots \dots \dots (5)$$

Let there be  $N$  free electrons in unit volume of the metal. Then the radial current in the disk is

$$C = \frac{\pi dae^2 \lambda N}{mv}.$$

Substituting the value of  $a$ , we get

$$\tau = \frac{2mv}{e^2 \lambda N}.$$

Let  $T$  be the free time of an electron so that  $\lambda = vT$ . The specific resistance of the metal is then given by

$$\tau = \frac{2m}{e^2 T N} \dots \dots \dots (6)$$

This is the same expression for the specific resistance which is obtained by considering the flow of electrons along a straight bar.

Now suppose that the disk, carrying the radial current  $C$ , is placed in a uniform magnetic field of intensity  $H$ , at right angles to the plane of the disk. Let the directions of  $r$ ,  $\theta$ ,  $H$  form a right-handed system.

The equations of motion of an electron are :

$$m \left\{ \frac{d^2 r}{dt^2} - r \left( \frac{d\theta}{dt} \right)^2 \right\} = \frac{ae}{r} + He r \frac{d\theta}{dt},$$

$$\frac{m}{r} \frac{d}{dt} \left( r^2 \frac{d\theta}{dt} \right) = -He \frac{dr}{dt},$$

where, of course,  $e$  must be taken as negative for the electrons. In the second of these equations for  $\frac{dr}{dt}$  we may put the average velocity acquired by the electron under the electric force alone, since the effect of the magnetic field is small. This average radial velocity is given by (5).

We thus find :

$$r^2 \frac{d\theta}{dt} = -\frac{1}{2} \frac{He^2 T a d}{m^2} + B.$$

At the beginning of a free path, when  $t=0$ ,  $r \frac{d\theta}{dt} = 0$  on



the average since the electromagnetic force has not had time to act on the electron. So  $B=0$ . At the end of a free path  $t=T$ . Thus the average tangential velocity acquired by an electron during its free path is

$$r \frac{d\theta}{dt} = - \frac{He^2 T^2 a}{4m^2 r}.$$

The whole circular flowing is :

$$I = - \int_{r_1}^{r_2} \frac{HNe^3 T^2 a d}{4m^2} \frac{dr}{r} = - \frac{HeTC}{4\pi m} \log \frac{r_2}{r_1}. \quad \dots (7)$$

This current changes in sign with the radial current  $C$ . Since  $e$  is negative, the current  $I$  is positive if  $C$  is directed outwards from the centre and negative if directed inwards. In the former case the circular current in the disk has the same direction as the magnetizing current, and in the latter case it has the opposite sign.

This circular current was measured by Professor Corbino in a bismuth disk by determining the current induced in a concentric coil of wire outside the disk when the radial current was made or broken. The direction of the current was found to agree with that given by this view of the effect. In order to obtain a uniform radial current a copper wire which passed through a hole in one pole-piece of the electromagnet was fastened to the centre of the disk. A copper ring was joined to the periphery of the disk and to this ring a circular copper plate was joined parallel to the disk. A copper tube enclosing and insulated from the central wire was joined to the centre of the copper plate. This method made it certain that the current introduced into the disk was wholly radial. Nothing is said in his paper of making a radial slit in the circular copper plate. Unless this were done, the effect of the circular current in the bismuth plate would be partly balanced by the effect of the opposite current in the copper plate. He states that when the bismuth plate was replaced by a copper plate no effect was observed. This is just the result to be expected if no radial slit to prevent a circular current were made.

If we assume, however, that the whole effect obtained was the result of the circular current in the bismuth plate, this experiment gives a simple method of calculating the free time of an electron in bismuth. For a radial current  $C=15$  amperes in a magnetic field of 3700, the circular current  $I$  was found to be 0.26 ampere. The radius  $r_2$  of the disk was 3.25 cm. The radius  $r_1$  of the copper wire is not given,

but it is reasonable to suppose that it was such that  $\frac{r_2}{r_1} = 15$ . Using these values in eq. (7) with  $\frac{e}{m} = 10^7$  we find

$$T = 2 \cdot 10^{-12}.$$

The specific resistance of bismuth is

$$\tau = 1.3 \cdot 10^4,$$

$$e = 1.6 \cdot 10^{-20}.$$

Eq. (6) thus gives for the number of free electrons in unit volume of bismuth :

$$N = 5 \cdot 10^{20}.$$

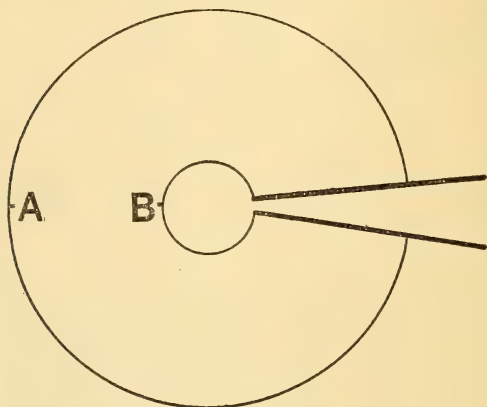
It was found that the circular current was not proportional to the magnetic field, but increased less rapidly than the magnetic force. But there are reasons (Phys. Review, xxiv. p. 428, 1907) for believing that the free time of an electron is dependent upon the magnetic force, and this may account for the differences observed between theory and experiment.

Professor Corbino regards this effect of the magnetic field upon the current in the disk as something distinct from the Hall effect. It is certainly true that if the Hall effect is defined as a bending of the equipotential lines by the magnetic field, then this effect is different. For in this case the equipotential lines are concentric circles both in and out of the magnetic field. It seems to me, however, that the effect described by Professor Corbino is, essentially, the Hall effect, but measured in a different way from that usually employed. In fact, his method seems to be the ideally simplest way to measure the Hall effect. In the ordinary method, where a uniform current is sent through a rectangular plate, and the transverse current is led out at two points, complications in the current distribution in the plate are introduced which make it difficult to apply the electron theory of metallic conduction. Experiments are now in progress here to measure the effect in a number of metals in addition to bismuth.

The view that Professor Corbino's effect is really the Hall effect receives support when we examine the inverse case. Suppose a circular current flows through a disk in a magnetic field. A radial current should result. In order to introduce a circular current into the disk the arrangement

shown in the accompanying figure might be adopted. A sector of small angle is cut out of the disk and two wires of

Fig. 1.



very low resistance soldered to the edges. If the current is introduced through these wires, then, if their resistance can be neglected, it may be shown that the circular current density in the disk is inversely proportional to the radius; there is no radial current. The equipotential lines are the radii. Now apply a magnetic field perpendicular to the disk. Obviously it is impossible to lead out the radial current so as to make this experiment the exact inverse of the former one. The best that can be done is to connect the extremities, say A, B, of a radius to a galvanometer which will show that these points are no longer at the same potential. But this effect is certainly the Hall effect. The rectangular plate ordinarily employed has only to be thought of as bent and stretched into the form shown.

For the theory of the two other electromagnetic effects, we shall follow Professor Corbino's argument, but expressed in terms of the characteristics of the electrons. Suppose the disk carrying the radial current  $C$  is suspended in a uniform magnetic field so that its normal makes an angle  $\phi$  with the lines of force. The energy of the disk in the magnetic field is given by

$$W = -\frac{1}{2} \int_{r_1}^{r_2} \frac{H N e^3 T^3 a d}{4 m^2 r} \pi r^2 dr H \cos^2 \phi,$$

assuming the magnetic permeability to be unity.

Hence

$$W = - \frac{eH^2 CTS}{16\pi m} \cos^2 \phi,$$

where  $S$  is the effective area of the disk.

Thus the torque on the disk is

$$-\frac{\partial W}{\partial \phi} = - \frac{eH^2 CTS}{16\pi m} \sin 2\phi.$$

The existence of this torque was shown, but not measured, by Corbino in the case of bismuth. Its measurement would furnish another means of calculating the free time of an electron.

The third effect, the induction of a radial current in the disk on exciting a normal magnetic field, is also easily explained. At any instant during the rise of the magnetic field let  $E$  be the radial electromotive force and  $c$  the radial current. Then

$$\frac{dW}{dt} = Ec = - \frac{ecS}{16\pi m} \frac{d}{dt} (H^2 T).$$

We assume that  $T$  is a function of the magnetic force.

Therefore :

$$E = - \frac{eS}{16\pi m} \frac{d}{dt} (H^2 T).$$

The resistance of the disk is

$$R = \frac{\tau}{2\pi d} \log \frac{r_2}{r_1}.$$

Hence the whole quantity of electricity that flows radially during the setting up of the magnetic field is :

$$Q = - \frac{eS}{16\pi m R} H^2 T.$$

On comparison with the theory of these effects given by Professor Corbino, we see that his "differential moment of the ions,"  $E''$ , is to be replaced by

$$\frac{1}{2} \frac{eT}{m}.$$

For the field strength 3700, Professor Corbino determined



this by experiment from the third effect to be  $1.54 \cdot 10^{-5}$  \*. Hence

$$T = 3 \cdot 10^{-12},$$

which is in good agreement with the value  $T = 2 \cdot 10^{-12}$  found from the first effect.

XXVII. *Analysis of the  $\gamma$  Rays from the Uranium Products.*  
By H. RICHARDSON, M.Sc., Beyer Fellow, University of Manchester †.

IN previous papers ‡ it has been shown that the  $\gamma$  rays emitted by the radium, thorium, and actinium products can be analysed into groups of different penetrating powers. All the radioactive substances which emit  $\beta$  rays have been examined except the uranium products, viz. uranium X<sub>1</sub> and uranium X<sub>2</sub>. In order to complete the series the analysis of the  $\gamma$  rays from these substances has been undertaken, and confirmatory evidence concerning the atomic weight of actinium has been obtained.

The uranium X used in the experiments was separated from 3 kilograms of pure uranium nitrate. The method of separation employed was that used by Soddy and Russell § in their early investigations on the penetrating power of the  $\gamma$  rays from uranium X. It consists in the fractional crystallization of the uranium nitrate from a solution of density 2.06. Under these conditions, the uranium nitrate which crystallizes out only carries with it about one-seventh of the total amount of uranium X present, and the remaining six-sevenths may be poured off with the mother liquor. By repeating this process about three-quarters of the uranium X can be obtained in a solution which contains only a few grams of uranium nitrate. The uranium X was finally separated by precipitation with ammonia and ammonium carbonate in the presence of ferric chloride. By this means the uranium X was obtained together with a small amount of ferric hydroxide, and the whole source thus consisted of

\* The value given by Professor Corbino for E is  $7.7 \cdot 10^{-5}$ . This is to be multiplied by 2 on account of an error corrected in the second of his papers referred to; and it should be divided by 10 since in another place he has used the ampere as the unit of current instead of the absolute unit.

† Communicated by Prof. E. Rutherford, F.R.S.

‡ Rutherford and Richardson, *Phil. Mag.* xxv. p. 722 (1913), xxvi. p. 324 (1913).

§ Soddy and Russell, *Phil. Mag.* xviii. p. 620 (1909).

a very thin layer of material. The purity of the uranium X used was tested by measuring its rate of decay.

As the apparatus and method used in the experiments were the same as those previously employed\*, it is not necessary to give details. It may be pointed out, however, that, as the amount of uranium X in equilibrium with one kilogram of uranium nitrate corresponds in  $\gamma$  ray activity to only about .01 mgrm. of radium, the activities obtained were very small and consequently the absorption coefficients could not be measured with great accuracy.

The absorption curves, using aluminium as the absorbing substance, were obtained and analysed in the usual manner.

Fig. 1.

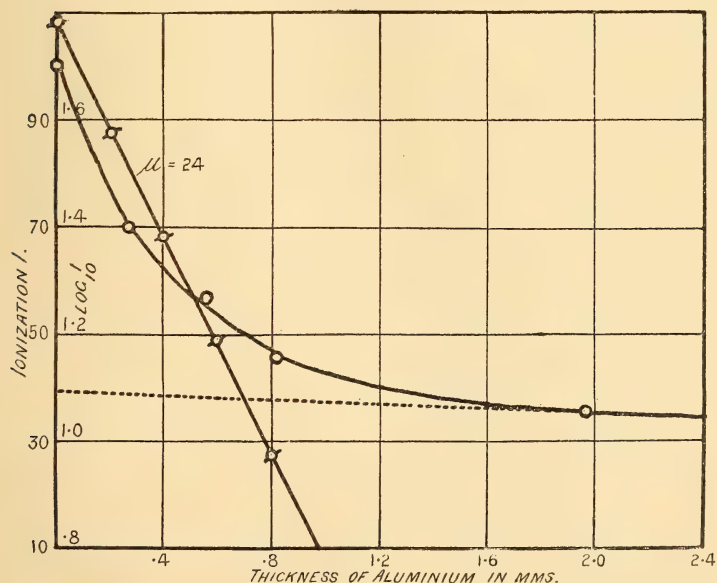


Fig. 1 shows the initial portion of the curve. It will be seen from the figure that about 40 per cent. of the total radiation is absorbed by 2 mm. of aluminium. The absorption, as shown by the logarithm curve, is exponential, the absorption coefficient  $\mu$  in aluminium being 24 (cm.)<sup>-1</sup>.

The determination of the absorption curve for greater thicknesses of aluminium was a matter of some difficulty owing to the very small activity (0.3 div. min. initially) at my disposal. It was for this reason impossible to obtain the

\* Rutherford and Richardson, *Phil. Mag.* xxvi. p. 324 (1913).

curve for thicknesses of aluminium greater than 5 cm. The numbers obtained over this range clearly indicated, however, that this more penetrating radiation is complex, consisting of two types. This view is supported by the work of Soddy and Russell\*, who have previously examined in detail the absorption of the penetrating  $\gamma$  rays from uranium X, using large thicknesses of aluminium. They separated the uranium X from 50 kilograms of uranium nitrate, and with this amount of active material they were able to follow the absorption through 12 cm. of aluminium. Their work was specially directed to determine the absorption coefficient of the residual radiation after passing through 2 cm. of aluminium. They were able to show that after a thickness of 5 cm. the absorption curve was quite exponential. The exact value of the absorption coefficient which they obtained varied slightly according to the particular experimental disposition which they employed. The extreme values of the absorption coefficients in aluminium which they obtained were  $\mu = \cdot 130$  and  $\mu = \cdot 148$ . From an inspection of the curves given by Soddy and Russell it is at once seen that a soft type of radiation was also present which was practically absorbed by a thickness of 5 cm. of aluminium. The absorption curve I obtained between 4 mm. and 5 cm. appeared to be in good agreement with the results given by the above curves. I have therefore based the analysis of the absorption curve, shown in fig. 2, on the assumption that the most penetrating type of radiation is that observed by Soddy and Russell. Assuming, with sufficient accuracy, a mean value of the absorption coefficient  $\mu = 0\cdot 140$ , the analysis of the absorption curve between 4 mm. and 5 cm. shows that the other type of radiation has an absorption coefficient  $\mu = 0\cdot 70$  and that it is exponentially absorbed. As the examination of the absorption of the penetrating  $\gamma$  rays from uranium X had been made with great care by Soddy and Russell, it did not seem necessary in these experiments to repeat any of their work.

It has been shown that uranium X emits  $\gamma$  rays consisting of three types which have absorption coefficients  $\mu = 24$ ,  $\mu = 0\cdot 70$ , and  $\mu = 0\cdot 140$  in aluminium of density 2.72.

The recent work of Fajans and Göhring†, Hahn and Meitner‡, and Fleck§ has shown conclusively that uranium

\* Soddy and Russell, *Phil. Mag.* xviii. p. 620 (1909).

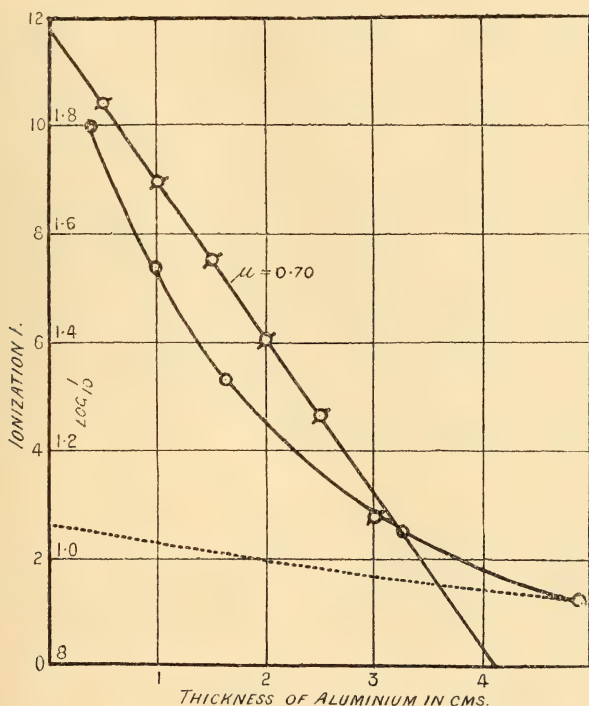
† Fajans and Göhring, *Die Naturwissenschaften*, Heft xiv. p. 339 (1913).

‡ Hahn and Meitner, *Phys. Zeit.* xvi. p. 758 (1913).

§ Fleck, *Phil. Mag.* xxvi. p. 528 (1913).

X is not a simple product but that it consists of two bodies, viz. uranium  $X_1$  and uranium  $X_2$ . Uranium  $X_1$  has a period of 24.6 days and emits soft  $\beta$  rays, and uranium  $X_2$  has a period of 1.1 mins. and emits hard  $\beta$  rays. It is quite impossible

Fig. 2.



without using a very large amount of material to settle definitely to which of the various products the various types of  $\gamma$  rays belong. Evidence on this point may be obtained, however, by a consideration of the penetrating power of the  $\gamma$  rays emitted by radium B, radium C, thorium B, thorium D, actinium B, and actinium D. Previous work has shown that each of the B products emits three types of soft  $\gamma$  rays, whilst radium C, thorium D, and actinium D each emit only one single penetrating type. It has also been pointed out that those bodies which emit soft  $\gamma$  rays also in general emit a soft  $\beta$  radiation.

It would appear therefore reasonable to suppose that uranium  $X_1$  emits those rays for which  $\mu = 24$  and  $\mu = 0.70$ , since these groups correspond to two of the groups emitted



by radium B, thorium B, and actinium B. The single penetrating type of radiation for which  $\mu = 0.140$  would then be due to uranium  $X_2$ . Under these conditions the  $\gamma$  rays emitted by uranium  $X_1$  and uranium  $X_2$  would appear to be quite analogous to those emitted by the other members of the radioactive series.

Attention has already been drawn to the fact \* that those radiations which correspond to the "L" series of Barkla seem to persist throughout the whole series of radioactive substances, with the exception of the D products. The radiation for which  $\mu = 24$  and which appears to be emitted by uranium  $X_1$  evidently belongs to the "L" series. This result gives additional evidence that the atomic weight of actinium is about 230 and that actinium is probably a branch product of the uranium series. Fleck † has already pointed out that the branch cannot come from uranium  $X_2$ . Now previous work has shown that in the case of radium C and thorium B, branch products occur either immediately before or after the emission of a single penetrating type of  $\gamma$  radiation. If we assume that the actinium branch comes from uranium  $X_1$ , then the analogy with the other radioactive bodies would be complete.

### *Summary.*

It has been shown that uranium X, by which are denoted the products uranium  $X_1$  and uranium  $X_2$  in equilibrium, emits three types of  $\gamma$  rays having absorption coefficients in aluminium  $\mu = 24$ ,  $\mu = 0.70$ , and  $\mu = 0.140$  (cm.)<sup>-1</sup>. Evidence has been given that the first two types are probably emitted by uranium  $X_1$  whilst the third penetrating type is due to uranium  $X_2$ .

The results obtained support also the view that the atomic weight of actinium is about 230 and that actinium is probably a branch product from uranium  $X_1$ .

My best thanks are due to Professor Rutherford for his kind interest and constant help throughout the course of these experiments.

University of Manchester,  
December, 1913.

\* Rutherford and Richardson, Phil. Mag. xxvi. p. 937 (1913).

† Fleck, Phil. Mag. xxvi. p. 528 (1913).

XXVIII. *On the Structure of the Atom.*  
*By Professor W. PEDDIE\*.*

§ 1. *The present Aspect of the Problem.*

THE strongly marked violation of the doctrine of equipartition of energy which is made evident in the phenomena of radiation, together with the violation of the Newtonian dynamics which it seems at first sight to imply, has given rise to the idea of discontinuity of transferences of energy; and a highly approximate empirical representation of the distribution of energy in the spectrum has led to the postulate of a unit of energy as an actual physical entity. But the fact that this unit is a variable, dependent on the frequency, naturally raises doubts as to the physical reality of units separately or superposably located in æther. Though the existence of energy, in association with particular phenomena, in definite multiples of definite units, is an experimental fact, an obviously alternative supposition to the above one is that any emission or absorption of energy in multiples of definite quantities which actually occurs is due to structural peculiarities of the emitting or absorbing mechanism. This is a point which must not be overlooked in spite of the great success as a working hypothesis, in other departments of physics besides that of radiation, of the idea of unitary transmission of energy. The most recent success in the department of radiation has been made by Dr. Bohr (Phil. Mag. 1913, July, Sept., Nov.) in the application of the  $h\nu$  postulate to the deduction of the formulæ for line spectra.

In the course of the discussion on spectra at the 1912 meeting of the British Association, I stated that the origin of spectrum series could be found rather in a complicated structure of the atom itself, than in complexity of structure of configurations of electrons circulating in or round a comparatively simple atomic structure. It is well known that great difficulties beset the deduction of the laws of series on the latter basis. I pointed out that, on the former basis, such difficulties do not exist; that any spectrum can be accounted for; that, with rotating spherical distributions of electricity, variations of spectra under different physical conditions can be accounted for; and that there are sufficient disposable quantities to provide for observance of the laws regulating emission of electrons under the action of Röntgen rays or ultra-violet light. The full discussion is given here.

\* Communicated by the Author.

In Dr. Bohr's investigation the characteristic formulæ for series are deduced in a beautifully direct manner, on the postulate of the existence of energy quanta, and in connexion with Rutherford's modification of the type of atom in which electrons are supposed to circulate in rings around a central nucleus. This leads to the usual impossibility of reconciling certain actions with the laws of ordinary dynamics and electrodynamics. In such cases, without specification of the details of a suitable new dynamics, merely on the ground of transference of energy in quanta, very simple explanations of fundamental phenomena in modern physics are obtained. The value of the new ideas as a working hypothesis cannot be denied. But behind all this procedure there lies the root question whether or not the peculiarities, so readily explained on the new ideas, cannot be explained in terms of the ideas of the older physics as consequences of structural conditions. For example, structural conditions can account for the non-entrance, at ordinary temperatures, of more than five of the freedoms of a molecule of a diatomic gas in interchanges of energy amongst the molecules; and thus a violation of the doctrine of equipartition of energy amongst the freedoms can take place without violation of the laws of ordinary dynamics. Similarly, it may be that structural conditions compel, in certain cases, the emission or absorption of energy in quanta without the existence of definite indivisible units of energy, and that they also introduce a limitation on the effective phases or complexions whose full presence is essential to the deduction of the law of equipartition from the doctrine of chance in combination with the Newtonian laws of motion.

Sir J. J. Thomson has recently (*Phil. Mag.* Oct. 1913) described an atomic mechanism which would account for many of the peculiarities under discussion. Along with a radial action, uniform in all directions round the atom, he postulates another radial action confined to definite tubes. The expulsion of an electron is effected by the absorption of radiant energy under the condition of resonance. The difficulty, whatever it be, of explaining the necessary magnitude of the absorption with resonance seems to exist, in this case, as strongly as in others to which objection has been raised on that ground. The primary purpose in introducing this type of atom was to obtain a ready explanation of the smallness of the amount of ionization produced, per unit volume of a gas, by means of Röntgen rays. The type described below possesses this property and yet enables us to retain the notion of a continuous wave-front. In the former, the

electrons do not revolve around a nucleus; in the latter, as in Dr. Bohr's scheme, they may so revolve. In the latter, bright line emission may arise from the revolution of electrons in the steady state; in Dr. Bohr's scheme there is no emission, or practically none, in steady states, bright lines being due to vibrations induced—in a manner not specified because it is not within the scope of ordinary dynamics—by the passage of the system from one steady state to another.

Though all such possibilities ought to be considered, for they are directly suggested by actual phenomena, it does not seem to me that we are yet under compulsion to forsake the laws of ordinary dynamics in connexion with atomic properties, or the doctrine of a continuous wave-front in æther, or even, apart from magnetic action, the notion of central symmetry in atomic action.

## § 2. A centrally symmetrical Atom.

To meet the condition of stable circulation of electrons we must have regions of attractive force. To meet the conditions of expulsion of electrons, *without necessary absorption of much radiational energy*, we must have regions of repulsive force alternating with the former; and the total work done by the forces of repulsion on an ejected electron must exceed that done on it by the attractive forces by the amount necessary in order to account for the speed of ejection. The law of radial variation of force must be such as to account for any observed spectrum series.

Subject to these conditions many different structural arrangements may be postulated. We are not necessarily bound down to the law of repulsion according to the inverse cube of the distance, or to constancy of angular momentum of the electrons. On other bases, different interpretations of the dynamical significance of Planck's constant  $h$  from that given by Nicholson would be furnished. But it is of interest to discuss the spherical counterpart of the tubular atom of Sir J. J. Thomson (Phil. Mag. Oct. 1913).

Let there be relatively broad regions in which the law of radial acceleration is

$$m\ddot{r} = \frac{Ae}{r^3},$$

$e$  and  $m$  being the charge and mass of an electron. The volume density of a distribution of electricity giving rise to this is  $\rho = +3A/4\pi r^4$  outside an interior radius  $\alpha$  which includes within it an amount of negative electricity equal to  $A/\alpha$ . If now, over the spherical surface of radius  $r_n' > \alpha$ ,



there is uniformly distributed a charge  $A/r_n$  of positive electricity, while an equal negative charge is distributed over the shell of radius  $r_n''$ , where  $r_n' < r_n < r_n''$ , there will be no resultant force at  $r_n$ ; and, in the region between  $r_n'$  and  $r_n''$ , the force will be towards  $r_n$ . The frequency of radial vibration of an electron at  $r_n$  is  $\nu_n$  where

$$2\pi\nu_n = \sqrt{\frac{Ae}{m} \cdot \frac{1}{r_n^2}}.$$

Outside  $r_n''$  the field is  $A/r^3$  as before; and the process of construction may be repeated for a whole series of values of  $n$  corresponding to any given spectrum series.

To obtain, for example, Balmer's hydrogen series we must determine the  $r$ 's by the condition

$$\sqrt{\frac{Ae}{m} \cdot \frac{1}{r_n^2}} = 2\pi C \left( \frac{1}{p_1^2} - \frac{1}{p_n^2} \right),$$

where  $C = 3 \cdot 29(10)^{15}$ ,  $p_1 = 2$ ,  $p_n = n$  which is any integer from 3 onwards.

In the region between  $r_n$  and  $r_n''$  an electron can circulate with a frequency  $\nu_n'$  given by

$$2\pi\nu_n' = \sqrt{\frac{Ae}{m} \cdot \frac{1}{r_n^2}} \sqrt{\frac{\xi}{r_n}},$$

where  $\xi$  lies between 0 and  $r_n'' - r_n$ . If  $\nu_n$  represents a frequency in the visible spectrum,  $\nu_n'$  must correspond to a frequency far outside the visible spectrum at the red end if  $r_n'' - r_n'$  is very small in comparison with  $r_n$ , and extending to infinity as the energy of revolution is radiated away. If, further,  $r_n'' - r_n'$  is very small in comparison with  $r_{n+1} - r_n$  or  $r_n - r_{n-1}$ , a very small proportion of the electrons which are projected into the atom from the outside can be retained. The great majority are scattered, some at low, some at high, angles. Only those which strike the atom almost centrally can be retained, and of them, indeed, only a small proportion.

Because of the smallness of  $r_n'' - r_n'$ , the energy of an electron approaching the atom radially must be practically equal to  $\pi \sqrt{Aem} \cdot \nu_n$  if it is to reach the region  $r_n$ . Identifying this with  $h\nu_n$ , as Sir J. J. Thomson does (*loc. cit.*), we get  $A = 10^{-17}$ . Thus the quantum  $h\nu_n$  of energy disappears, taking the form of potential energy, before the radiation of frequency  $\nu_n$  can be excited.

On the other hand, the absorption of a very small amount,  $\frac{1}{2} \frac{Ae}{r_n^4} (r_n'' - r_n')^2$ , of energy in the form of radiation of frequency  $\nu_n$ , will liberate the electron, and cause the re-conversion of its potential energy into the kinetic energy with which it escapes from the atom. Thus we obtain a complete explanation of the readiness with which weak ultra-violet light or Röntgen radiation can liberate electrons possessing the quantum of energy. The quantum is not absorbed from the radiation, it is absorbed from the energy of the electron when it enters the atom and is stored for future use.

Using Whiddington's result that the kinetic energy of a cathode particle, exciting the hardest Röntgen radiation in an atom of atomic weight  $\varpi$ , cannot be less than  $\frac{1}{2} 10^{16} \varpi^2 m$ , we get

$$\frac{1}{2} 10^{16} \varpi^2 m \geq h\nu.$$

Hence  $\nu \geq 6.77 (10)^{14}$ , the actual value being  $8.2 (10)^{14}$ . In the case of a helium atom we find  $\nu \geq 1.08 (10)^{16}$ .

As in Professor Thomson's investigation, the energy of the pulse radiation is proportional to the square of the frequency in consequence of repulsion effectively inversely proportional to the cube of the distance, which is in accordance with observation. That law of repulsion also leads to a formula for the distribution of energy in the spectrum, which has been shown to possess some correspondence with fact (Sir J. J. Thomson, Phil. Mag. July 1910).

A similar construction can be imagined with any desired law of repulsion. In particular the law of repulsion requisite in order to give Planck's law for pulse radiation may readily be expressed by an infinite series. If  $F_1(r)$  be the law of repulsion, while  $F_2(r)$  is the law of attraction which is superposed upon it in the thin shells of thickness  $r_n'' - r_n'$ , we have

$$F_2'(r_n) e = F_1'(r_n) e + 4\pi^2 C^2 \left( \frac{1}{p_1^2} - \frac{1}{p_n^2} \right)^2,$$

where  $p_1$  and  $p_n$  are the constants of, say, the lines in Balmer's series,  $C$  being an absolute constant.

### § 3. An Atom characterized by axial Rotation.

In the preceding case, when the collisions are seldom, the spectrum is practically a line or band spectrum. The continuous radiation in the region of very great wave-length

will be feeble in comparison with that associated with the lines. But it is possible to have an atomic structure in which the line emission is produced by the revolution of the electrons in the interior of the atom, and not by their linear vibrations about fixed positions. In the preceding case the trouble is that, as radiation proceeds, the kinetic energy of the electron diminishes, and the electron gradually sinks in, with exhaustion of potential energy, to the region of infinitely slow revolution. In so far as this action is concerned, the spectrum of a glowing gas would be continuous. The trouble was avoided by banishment of the continuous part to a non-experimental range. There is only one way of practically avoiding it (see, however, § 5).

The energy of the radiation must be drawn from an internal store in the atom, the magnitude of which is very large in comparison with the circulatory energy of the electron itself. The positive electricity in the shell within which the electron circulates stably must itself be in rotation, and, if necessary, drag the electron with it. Thus the period of the circular vibration acquired is to some extent independent of the tangential component of the speed of an electron entering the atom from without. If  $\nu_n$  is the period associated with one of the shells, the condition for steady revolution of the electron is

$$\nu_n^2 = \frac{F_2(r_n) - F_1(r_n)}{4\pi^2 m r_n} e = C^2 \left( \frac{1}{p_1^2} - \frac{1}{p_n^2} \right)^2.$$

Hence the attraction within the shell is proportional to the distance from the centre. At the surface  $r=r_n'$ , a uniform surface distribution of positive electricity must be located, its amount being that requisite to raise the total charge within to the value

$$\frac{4}{3} \pi \rho_n r_n'^3,$$

where

$$\frac{4}{3} \pi \rho_n = 4\pi^2 \frac{m}{e} C^2 \left( \frac{1}{p_1^2} - \frac{1}{p_n^2} \right)^2.$$

At the surface  $r=r_n''$ , a uniform negative distribution must be placed, its amount being that required to make the force become a repulsion  $F_1(r_n'')$ : and so on. The shell of positive electricity within the range  $r_n'' - r_n'$  rotates round a central axis with angular velocity

$$\omega_n = 2\pi C \left( \frac{1}{p_1^2} - \frac{1}{p_n^2} \right),$$

in which the surface distributions may share.

If now we write

$$\frac{1}{2} m \omega_n^2 r_n^2 = q h \nu_n,$$

where  $h$  is Planck's constant and  $q$  is a numerical multiplier, we find

$$\frac{1}{r_n^2} = \frac{2\pi^2 m C}{q h} \left( \frac{1}{p_1^2} - \frac{1}{p_n^2} \right).$$

In Balmer's series  $p_1=2$  and the least value of  $p_n$  is 3. Thus the minimum value of  $r$  from which bright line radiation arises is

$$\frac{1}{\pi} \sqrt{\frac{2 q h}{m C}},$$

and the maximum value is  $3/\sqrt{5}$  times larger. With the data  $h=6.5(10)^{-27}$ ,  $m=8.8(10)^{-28}$ ,  $C=3.3(10)^{15}$ , we get as the minimum and maximum value respectively, on the assumption  $q=1$ , the numbers  $2.13(10)^{-8}$  cm. and  $2.86(10)^{-8}$  cm., which are quite in accordance with estimates of molecular magnitudes. The maximum is only twice as great as the value deduced for hydrogen from the observed density in the liquid state. Agreement would result if  $q=1/4$ .

It is of interest to consider conditions under which the value  $q=1/2$  would hold. If we write

$$m \omega_n^2 r_n = k_n r_n e$$

$$\frac{1}{2} m \omega_n^2 r_n^2 = 2\pi^2 m \nu_n^2 r_n^2 = q h \nu_n,$$

we find

$$k_n r_n e = \frac{q^2 h^2}{\pi^2 m^2} \cdot \frac{1}{r_n^3}.$$

Thus the attraction within each region  $n$ , of small breadth  $r_n'' - r_n'$ , is the attraction due to the law of the inverse cube of the distance from the centre of the atom. If this law is identical with the law of repulsion in the other regions we get

$$A = \frac{q^2 h^2}{\pi^2 m e}.$$

If now we also have

$$m \omega_n r_n^2 = a,$$

*i. e.* if angular momentum is conserved in the regions  $n$ , we get

$$a^2 = 2 m q h \nu_n r_n^2 = \frac{q^2 h^2}{\pi^2}.$$



Consequently, when an electron enters the atom from without with speed  $V$ , and attains radial rest in the region  $n$ , its energy is equally divided into potential energy and energy of circulatory motion, the magnitude of each being  $q\hbar\nu$ . But the total energy is  $h\nu_n$ . Therefore  $q=1/2$ , and the independently found condition  $q=1/4$  might result from closer approach of centres, during collision or under attraction in the liquid state, than to one full diameter. The same final result is attainable, however, if the intrinsic strength of the repulsion is three times greater than that of the attraction.

From the expression

$$\frac{1}{r_n^2} = \frac{2\pi^2 m C}{qh} \left( \frac{1}{p_1^2} - \frac{1}{p_n^2} \right),$$

together with the estimated value,  $3.7(10)^{-13}$  cm., of the diameter of an electron, we can calculate the maximum allowable value of  $p_n$  in Balmer's series on the assumption that  $r_{n-1} - r_n$  is not less than that diameter. If  $p_n=27$ ,  $r_n$  would be about  $2.10^{-8}$  cm.; if  $p_n=40$ ,  $r_n$  would be about  $3.10^{-8}$  cm., by the limitations  $r_{n-1} - r_n = 3.7(10)^{-13}$  and  $q=1$ . In accordance with the preceding estimate of the minimum and maximum radii, the value of  $p_n$  must lie within these extremes. The greatest observed value is 35. The same values follow if  $q=1/2$  and  $r_{n-1} - r_n$  equal to  $\sqrt{2}$  times the diameter of an electron.

But we must make  $r_{n-1} - r_n$  a considerable multiple of the diameter of an electron. It is really  $r_n'' - r_n'$  which must not be less than that diameter. If we make the multiple 100,  $q$  must be made equal to  $10^{-4}$  to give the same value of  $p_n$ . With 35 as the maximum value of  $n$ , we now find  $r_{35} = 2.62(10)^{-10}$  cm.; and the first line ( $n=2$ ) in the series originates at  $r_3 = 3.5(10)^{-10}$  cm.

#### § 4. *The Magnetic Field and the Magnetron.*

In the preceding discussion no account has been taken of the magnetic field due to the rotation of the electrification. The tangential component of the field due to the distribution  $\rho$  (§ 2) is

$$H_t = \frac{4}{3} \pi \sin \theta \int_a^r \rho_1 \omega_1 r_1 \left( \frac{r_1}{r} \right)^3 dr_1 - \frac{8}{3} \pi \sin \theta \int_r^\beta \rho_1 \omega_1 r_1 dr_1$$

where  $\beta$  is the external radius, if we regard the negative core as having no rotation. The condition of equilibrium of

a revolving electron is

$$H_t e \omega r = \frac{Ae}{r^2} + m \omega^2 r,$$

with the limitation  $\theta = \pi/2$ . This determines  $\omega$  as a function of  $r$ . The previous condition  $\nu :: 1/r^2$  could be satisfied if

$$H_t = B \omega, \quad \frac{Ae}{r^4} = (Be - m) \omega^2,$$

but, to attain this, other terms must be added to  $H_t$ , say terms due to surface distributions of electricity. We shall presume these to be so arranged as to give shells of small thickness within which stable circulation of an electron is possible. In all other regions the resultant force upon an electron is outwards. The resultant electric force acting upon it may always be outwards, the electrodynamic force alone being inwards.

An electron entering the atom with a moment of momentum opposed to that of the shells determining the field is then necessarily ejected. Ejection is then also the fate of any electron whose path is inclined at more than a very small angle to the equatorial plane of the atom. Even when this condition is satisfied, the angular momentum of the electron must not deviate much from that appropriate to one of the shells within which equilibrium is possible.

Let us presume, for the sake of simplicity, that the regions in which the electricity constituting the atom is in rotation round a common axis are very thin shells. Regarding one of these, of radius  $r_\mu$ , as being effectively a surface distribution of density  $\sigma_\mu$ , the radial component of the magnetic force on the shell of radius  $r_n$  is

$$H_r = \frac{8}{3} \pi \cos \theta \left[ \sum_1^{n-1} \omega_\mu \sigma_\mu r_\mu \left( \frac{r}{r_n} \right)^3 + \sum_{n+1}^m \omega_\mu \sigma_\mu r_\mu \right],$$

where  $m$  is the total number of shells. The sign of the quantity in brackets determines the stability of the shell if it be free to alter the direction of its axis.

The magnetic moment of a shell is  $\frac{8}{3} \pi^2 r^5 \omega \sigma$ . If this be an absolute constant, or a small integral multiple of an absolute constant, we have therein a physical basis for the magneton. And if different stable arrangements with direct or reverse alignment of the shells be possible, we have a condition under which fundamental changes in spectra may take place. If the internal field be sufficiently powerful, and it must in general be so regarded since the most powerful external fields at our disposal are effects of the same action

greatly diminished by distance, these changes will not readily occur, will occur only under special circumstances, and the effect of an external field on the emission of radiation will be slight. The axes of rotation of the shells will always, apart from slight vibrations due to disturbances caused by electrons or other atoms, be co-linear. The trouble arising from want of parallelism of the elementary magnets, which appeared for example in Ritz's model, does not arise in this system, which thus gives a ready explanation of that constancy of the magneton to which Weiss's work has given a fairly broad basis of experimental support.

No more than one stable condition is possible unless the number of shells exceeds three. In the case of four, if we write  $r_\mu^3/r_n^3 = 2_n A_\mu$ ,  $\omega_\mu \sigma_\mu \nu_\mu = \alpha_\mu$ , and  $\alpha_\mu$  for  $3/8\pi \cos \theta$  times the equatorial field acting on the  $\mu$ th shell, we have

$$\begin{aligned} 0 \cdot x_1 + x_2 &+ x_3 &+ x_4 &- \alpha_1 = 0, \\ {}_2A_1 \cdot x_1 + 0 \cdot x_2 &+ x_3, &+ x_4 &- \alpha_2 = 0, \\ {}_3A_1 \cdot x_1 + {}_3A_2 \cdot x_2 + 0 \cdot x_3, &&+ x_4 &- \alpha_3 = 0, \\ {}_4A_1 \cdot x_1 + {}_4A_2 \cdot x_2 + {}_4A_3 \cdot x_3, &+ 0 \cdot x_4 &- \alpha_4 = 0. \end{aligned}$$

If we reverse  $x_\mu$  we must reverse  $\alpha_\mu$ . Hence no case with one  $x$  reverse and the others direct is possible.

Now consider the moments of all the shells to be equal and write  $x_2 = px_1$ ,  $x_3 = qx_1$ ,  $x_4 = rx_1$ . The conditions are

$$\begin{aligned} 0 + p &+ q &+ r &- \alpha_1' = 0, \\ p^{\frac{3}{4}} + 0 &+ q &+ r &- \alpha_2' = 0, \\ q^{\frac{3}{4}} + \left(\frac{q}{p}\right)^{\frac{3}{4}} + 0 &+ r &- \alpha_3' = 0, \\ r^{\frac{3}{4}} + \left(\frac{r}{p}\right)^{\frac{3}{4}} + \left(\frac{r}{q}\right) + 0 &- \alpha_4' = 0, \end{aligned}$$

and

$$1 > p > q > r.$$

With the second and third terms, and therefore  $\alpha_2'$  and  $\alpha_3'$ , negative, the first equation cannot be satisfied; with the second and fourth terms, and therefore  $\alpha_2'$  and  $\alpha_4'$ , negative, the second equation cannot be satisfied. Similarly, if the third and fourth terms are negative, the third equation cannot be satisfied; and the first condition prevents the second, third, and fourth terms from being negative simultaneously. So only one stable arrangement (all terms involving  $p$ ,  $q$ ,  $r$  positive) is possible with four, as with three, shells provided that the magnetic moments of the four are

equal. But a second stable arrangement can be found if the moments are not all equal. Let the ratios of the moments be  $1 : k : k' : k''$ . If  $r_1, r_2, r_3, r_4$  be the radii of the shells, the conditions are

$$0 + k\left(\frac{r_1}{r_2}\right)^4 + k'\left(\frac{r_1}{r_3}\right)^4 + k''\left(\frac{r_1}{r_4}\right)^4 - \alpha_1' = 0,$$

$$\left(\frac{r_1}{r_2}\right)^3 + 0 + k'\left(\frac{r_1}{r_3}\right)^4 + k''\left(\frac{r_1}{r_4}\right)^4 - \alpha_2' = 0,$$

$$\left(\frac{r_1}{r_3}\right)^3 + \left(\frac{r_2}{r_3}\right)^3 + 0 + k''\left(\frac{r_1}{r_4}\right)^4 - \alpha_3' = 0,$$

$$\left(\frac{r_1}{r_4}\right)^3 + \left(\frac{r_2}{r_4}\right)^3 + \left(\frac{r_3}{r_4}\right)^3 + 0 - \alpha_4' = 0.$$

Taking the third and fourth terms as negative, and therefore  $\alpha_3'$  and  $\alpha_4'$  negative, we have, for example, with  $r_1/r_2 = 0.98$ ,  $r_1/r_3 = 0.5$ ,  $r_1/r_4 = 0.49$ ,  $k' = 1$ ,  $k = k'' = 5$ , a stable arrangement which is non-magnetic.

We have thus a model of an atom which may be either magnetic or non-magnetic. Although it may be the case that most examples of the non-magnetic condition of substances which can exhibit magnetic quality may arise from counteraction of the effects of individually magnetic atoms, the possibility of counteraction of the effects within the atom itself must be considered.

In the preceding discussion the magnetic action of the electrification within the thin shells has not been entered upon. The distribution of electrification within them may be such as to give rise to satellite lines and the observed peculiarities of the Zeeman effect.

Radioactivity may be caused by slowing down of the angular velocities of the shells producing re-arrangement of the alignment of axes. Under sufficient shock it might be conceivably possible for ejection of a series of shells to take place—an  $\alpha$  particle or helium atom, for example, being driven out.

One different type of radiation might arise from vibrations of the axes of the individual shells, another from displacement of their centres.

The proof of the statements made on p. 265 regarding equilibrium and ejection of atoms is as follows. The expression for the radial and tangential components of the magnetic field being respectively written as  $N \cos \theta$  and



$M \sin \theta$ , radial equilibrium ensues if

$$\frac{Ae}{r^3} - Me\omega r \sin^2 \theta + m\omega^2 r \sin^2 \theta = 0,$$

and tangential equilibrium ensues if

$$Ne = m\omega,$$

or if  $\theta = 0$  or  $\theta = \pi/2$ . If at  $\theta = \pi/2$  there is equilibrium, the former condition becomes

$$\frac{Ae}{r^3} + m\omega^2 r = Me\omega r = He\omega r,$$

as already found, and the radial force is one of repulsion at any other value of  $\theta$  with the same  $r$ . Whenever  $\omega$  slows down sufficiently by radiation, expulsion follows. It is quite possible to arrange equilibrium at a value of  $\theta$  other than  $\pi/2$ , but continuous decrease of  $\omega$  would then occur with continuous increase of  $\theta$ .

### § 5. *Addendum.*

In order to account specially for the laws observed to regulate the expulsion of electrons by photoelectric action or by Röntgen rays, the requisite law of electrostatic repulsion has been adopted, and no special case of electric attraction has been considered in conjunction with the electromagnetic action. A paper by Professor Conway has appeared in a recent issue (Dec.) of the *Philosophical Magazine*, in which results of electrostatic attraction have been considered, and a very remarkable mode of preserving constancy of period has resulted, while emission of radiation may proceed by quanta. Such emission does not occur in the cases considered above, but there is no experimental basis necessitating provision for this condition in bright line emission. If such a basis arose electrostatic attraction might have to be postulated in the regions of stable revolution of electrons.

The fundamental difference between Professor Conway's scheme and the above one lies in the origin of stable regions. He seeks it in nodal oscillations of the atom, that is in the qualities which determine atomic vibrations. In the above treatment, it is sought for in the qualities of electricity or æther which determine, it may be, loci of permanent strain, or, in any case, features of permanent atomic structure.

XXIX. *Energy required to Ionize a Molecule by Collision.*  
*By J. S. TOWNSEND, Wykeham Professor of Physics, Oxford\*.*

IN the theory of ionization of gases by collision, it has been shown that the quantity  $\alpha$ , representing the number of molecules ionized by one electron in moving through a centimetre of the gas at a pressure of one millimetre, is given

by an equation of the form  $\alpha = N e^{-\frac{NE}{X}}$  for the larger values of the force  $X$ . The agreement between the formula and the experimental results was much closer than might have been expected, considering the assumptions which were made in finding the formula. Thus, for example, at the lower values of  $X$ , it has been found that the velocity of agitation of the electrons exceeds the velocity acquired under the force.

If the quantity  $\alpha$  represents the number of collisions with molecules in which the velocity of the ion exceeds a certain value  $V'$ , the velocity  $V'$  must be obtained on a different principle from that previously adopted, when the force  $X$  is small†. This may be illustrated by taking the values of  $\alpha$  recently obtained by Wheatley‡ for air corresponding to small values of the ratio  $X/p$ . The velocity of agitation  $u$ , and the velocity in the direction of the electric force  $W$ , for these values of  $X/p$ , have also been determined§.

For air at 1 millimetre pressure the values of  $\alpha$ ,  $u$ ,  $W$ , and  $k$  are given in the following table,  $k$  being the factor by which the kinetic energy of the electrons exceeds that of the surrounding molecules.

$X$ .	$\alpha$ .	$u \times 10^{-7}$ .	$W \times 10^{-6}$ .	$k$ .
40	019	9.1	15.0	81
50	055	10.1	17.3	100
70	212	11.3	22.0	125
90	495	12.2	25.5	150

The velocity of agitation of the molecules may be neglected in comparison with that of the electrons, and the mean free path  $l$  of an electron moving in air at 1 millimetre pressure may be taken as 0.32 centimetre.

\* Communicated by the Author.

† See 'Theory of Ionization of Gases by Collision,' p. 28.

‡ F. W. Wheatley, Phil. Mag. Dec. 1913.

§ J. S. Townsend & H. T. Tizard, Proc. Roy. Soc. lxxxviii. p. 336 (1913).

## 270 *Energy required to Ionize a Molecule by Collision.*

When an electron travels a distance of 1 centimetre in the direction of the electric force, the total length of its trajectory is  $u/W$  approximately (since  $u$  is large compared with  $W$ ), and the total number of collisions that it makes with molecules is  $u/Wl$ . The number that are ionized is  $\alpha$ , so that  $\alpha Wl/u$  is the ratio of the number of collisions in which the velocity of the electron exceeds  $V'$ , to the total number of collisions.

Let  $\phi(V)dV$  be the number of electrons moving with a velocity intermediate between  $V$  and  $V+dV$ . The total length of the paths they traverse per second is  $\phi(V)VdV$ , and the number of collisions in which the velocity of the electron is between  $V$  and  $V+dV$  is  $[\phi(V)VdV]/l$ .

The number of collisions  $N'$  in which the velocity of the electron exceeds  $V'$  is

$$\frac{1}{l} \int_{V'}^{\infty} \phi(V)VdV.$$

If the velocities are distributed according to Maxwell's law

$$\phi(V) \propto V^2 e^{-\frac{V^2}{b}},$$

and  $N'$  is proportional to

$$\int_{V'}^{\infty} e^{-\frac{V^2}{b}} V^3 dV.$$

The ratio  $N'/N$ , where  $N$  is the total number of collisions per second, is

$$\frac{N'}{N} = e^{-\frac{V'^2}{b}} \left( 1 + \frac{V'^2}{b} \right).$$

The quantity  $b$  is  $\frac{2c^2}{3}$  where  $c$  is the mean velocity of agitation. In the case of electrons moving in an electric field the kinetic energy of agitation exceeds that of the surrounding molecules by the factor  $k$  so that  $b = \frac{2kc_0^2}{3}$ ; where  $\frac{mc_0^2}{2}$  is the kinetic energy of agitation of a molecule of the gas. Hence equating  $\alpha Wl/u$  to  $N'/N$ , the value of  $V'^2/c_0^2$  is given by the following equation:—

$$\frac{\alpha Wl}{u} = e^{-\frac{3V'^2}{2kc_0^2}} \left( 1 + \frac{3V'^2}{2kc_0^2} \right).$$

The values of  $\alpha Wl/u$  for the different values of X are given in the following table, also the corresponding values of  $V'^2/c_0^2$  :—

X.	$\frac{\alpha Wl}{u}$ .	$\frac{V'^2}{c_0^2}$ .	P in volts.
40	$10^{-4}$	640	23.7
50	$3 \times 10^{-4}$	705	26
70	$1.3 \times 10^{-3}$	750	28
90	$3.3 \times 10^{-3}$	790	29

If  $V'$  be the velocity acquired by an electron in travelling freely between two points differing in potential by P volts, it is easy to show that  $\frac{V'^2}{c_0^2} = 27P$ .

The values of P thus obtained are given in the last column of the above table, the determination corresponding to the lowest value of X being the most reliable.

It thus appears that the energy required to produce ionization by collision in air is about  $23e/300$ ,  $e$  being the charge on the ion. This estimate of the energy is in agreement with that previously obtained by considering the larger values of  $\alpha$ .

It is remarkable that large alterations in the numbers given in the second column have very little effect on the values of P. It is only necessary, therefore, to know the values of  $\alpha$ ,  $l$ ,  $W$ , and  $u$  approximately, but the value of  $k$  must be known accurately, as an error in  $k$  would produce a proportional error in P.

XXX. *Air-Pressures used in Playing Reed Instruments.*  
By CHARLTON W. H. FOORD, *Mem. Royal Soc. of Arts*\*.

[Plate III.]

IN Dr. W. H. Stone's work 'Elementary Lessons on Sound' (Macmillan 1891) a table is given showing the maximum and minimum wind-pressures used in playing various wind instruments. The investigation of these pressures has been carried further by Dr. E. H. Barton and

\* Communicated by the Author.



Mr. S. C. Laws, in connexion with brass instruments with cup-shaped mouthpieces, viz.: the trumpet, cornet, and trombone; a full description of their most interesting experiments being reproduced in the 'Proceedings of the Physical Society of London,' vol. xviii., and also in the *Philosophical Magazine* for April 1902.

The experiments made by Dr. Barton and Mr. Laws upon the three instruments just referred to, showed that the tendency was for the wind-pressures to rise with a rise in pitch of the notes played. In Dr. Stone's table a similar rise of pressure with rise of pitch is indicated for every instrument which he mentions, except the clarinet, the other instruments being the oboe, bassoon, horn, cornet, trumpet, euphonium, and bombardon. The pressures, according to Dr. Stone, from the lowest notes to the highest notes on the clarinet varied from 15 inches of water to 8 inches, the clarinet thus displaying a remarkable peculiarity.

Dr. Stone's table of wind-pressures has been reproduced in several works by other writers, and some of these have assumed that the figures given by Dr. Stone for the clarinet were incorrect, two writers to the present author's knowledge having altered the figure 8 to 18 without making any comment, on the assumption, I suppose, that the figure 8 was a misprint. This curious disagreement between the wind-pressures for the clarinet as given by different writers, caused me to make a series of experiments with a view to verifying Dr. Stone's figures. These experiments were also extended to the saxophone, which is a brass instrument employing a mouthpiece and single reed similar to those employed on a clarinet, but having a conical bore and hence a scale corresponding with that of the oboe. That is to say, it "overblows" to the octaves of the fundamental tones, whereas the clarinet, which has a cylindrical bore, "overblows" to the twelfths. The word "overblows" is a convenient one in this connexion, but it will be seen from the following experiments that it is not literally correct when used in connexion with the single-reeded clarinet and saxophone.

The method followed in carrying out the experiments corresponds with that adopted by Dr. Stone and also by Dr. Barton and Mr. Laws. The pressures were taken by a water-manometer, similar to that used by organ-builders; connected to the mouth when playing by means of an india-rubber tube held in the corner of the mouth.

*Results of Experiments on the Clarinet.*

The instrument used for this purpose was a B $\flat$  Boehm system Clarinet tuned to the Low Pitch, and made by Hawkes & Son of London. A soft reed was used.

The results of scales extending through rather more than three octaves are given in Table I., and these results are graphically represented in Pl. III. headed "Clarinet." It will be seen that two sets of figures are given and two curves, one when playing as loudly as was consistent with a proper tone and the other when playing very softly.

TABLE I.  
*Pressures for Scales on B $\flat$  Clarinet.*

Notes.	Inches of Water.	
	Forte.	Piano.
E .....	15.5	6.5
F $\sharp$ .....	15	6.25
G $\sharp$ .....	14.5	6.25
A .....	14.5	6
B .....	14	6
C $\sharp$ .....	14	6
(D)		
D $\sharp$ .....	14	6
E .....	13.5	6
F $\sharp$ .....	13	6
G $\sharp$ .....	13	5.75
A .....	13	5.5
B .....	14	7
C $\sharp$ .....	13.5	7
D $\sharp$ .....	13	7
E .....	12.75	6.5
F $\sharp$ .....	12.25	6.5
G $\sharp$ .....	12.5	6.5
A .....	12	6
B .....	11.75	5.75
C $\sharp$ .....	11.5	5.75
D $\sharp$ .....	10.5	6
E .....	10.5	5.5
F $\sharp$ .....	10.5	5
G $\sharp$ .....	9.5	4.25

Mezzo-forte playing was also tried, but the results were found to be more uneven owing to the difficulty of maintaining the same degree of moderate intensity throughout a particular experiment. The figures given were considered the most representative after a number of experiments. In the graphical representation of the results the

ordinates of the curves are the manometer pressures in inches of water, this being the usual mode of measuring wind-pressures for organ-pipes ; while the abscissæ represent the musical intervals according to equal temperament. The D in brackets is middle C on the piano, the notes being as written for the instrument, and hence being a tone lower than the actual sounds produced, owing to the instrument being in B $\flat$ .

It will be seen, from an examination of the figures in the above table and the corresponding curves, that the general tendency is for the pressures to fall as the pitch rises. This result is the reverse of that recorded by Dr. Barton and Mr. Laws for the trumpet, cornet, and trombone, but agrees substantially with the figures for the clarinet given in Dr. Stone's original table. It will be noticed, however, that a temporary rise of pressure occurs at the second B $\sharp$ ; this note being the first note obtained after opening the twelfth or harmonic key and forming the first note of the so-called clarion register.

*Results of Experiments on the Saxophone.*

The instrument used for these experiments was an E $\flat$  alto Saxophone tuned to the high concert or military band pitch, and made by Hawkes & Son, London. The experiments to be described were made with the single reed proper to the instrument, and also with a bassoon reed which has double blades. The latter reed was adapted to the instrument by removing the mouthpiece and substituting a piece of cork hollowed out to carry the reed and fit the end of the instrument. The mode of tabulating and plotting the results is the same as that adopted for the clarinet. The A in brackets corresponds to middle C on the piano.

The results obtained with the saxophone are interesting, as they indicate that it is the form of reed which is the important element as regards the pressures employed in playing. It might be thought, from the figures in Dr. Stone's table (which does not include the saxophone), that as the only instrument there mentioned in which the pressures do not increase with rise of pitch is the clarinet, this peculiarity is confined to the clarinet and is perhaps due to its cylindrical bore. It will be seen, however, from an examination of the tables and curves for the saxophone when using the proper single reed, that the pressures at the beginning and end of the scales are practically equal, the maximum pressure, at any rate when playing loudly, being at the note D about half-way through the scale. It is at this note that

the new register begins, the octave key or keys being opened for all succeeding notes. It will be noted that this temporary rise of pressure at the commencement of the harmonic notes is also to be found on the curves for the clarinet.

TABLE II.

*Pressures for Scales on Eb Alto Saxophone.*

Notes.	Inches of Water.		
	Single Reed.		Double Reed.
	Forte.	Piano.	Forte.
B .....	10	6	14
C .....	10	5.5	13.5
D .....	10	5.8	13.5
E .....	11	5.75	13.7
F .....	11	5.5	13.5
G .....	11	6	13.7
(A) .....	11.5	6	14
B .....	11.5	6	13.7
C .....	12	5.5	14
D .....	14.7	6.5	15
E .....	14.5	6.25	15
F .....	14	6	15.5
G .....	13.5	6.5	17
A .....	13	6.6	19
B .....	12.25	6	23 at least
C .....	11	6	
D .....	10.5	5.75	
E .....	11	5.5	
F .....	11	5.5	

The results obtained when playing very softly on the saxophone shows that there is very little change of pressure required right through the entire compass of the instrument.

The third column of figures in Table II. and the uppermost curve on the saxophone chart (Pl. III.) show some results obtained by using a bassoon reed on the saxophone. Here we have a very different set of figures and form of curve, the pressures required for the higher notes being greatly in excess of those required for the lower notes, thus agreeing with the results shown in Dr. Stone's tables for the oboe and bassoon, and in addition all the other instruments in his table. The figures and curve indicate that but little modification of pressure is required for the fundamental notes, but after passing the middle D the pressures rapidly increase.



It may be remarked that when using the bassoon reed the lower notes were fairly readily produced and were of fairly good quality, very similar in fact to those obtained with the proper single reed and mouthpiece. The quality of the upper notes became bad however, and I was unable to obtain notes of proper intonation after the last B $\sharp$ . The figure 23, indicating the pressure for this note, must also be taken as only approximately correct since the note was very unsteady. It is quite conceivable that a bassoon player who would be better used to the control of a double reed could have obtained one or two higher notes.

### *Conclusions.*

The results of the above experiments are I think sufficiently consistent to support the figures for the clarinet in Dr. Stone's table, and to show that with a single reed or clarinet type of mouthpiece it is not necessary to increase the wind-pressure for the high notes of the instrument. I put forward the following suggestions in explanation of this seemingly curious result.

There are two important factors governing the pitch of a note produced by the aid of a reed upon a wind instrument, viz. :—Alteration of the vibrating length and alteration of the air-pressure. The first of these methods is most readily done by the performer's lips in the case of the single reed on a mouthpiece of the clarinet type, since the upper end of the reed, which rests on the lower lip when playing, is very delicate and vibrates to and from the bevelled face of the rigid mouthpiece. The bevelling is such that a wedge-shaped opening is provided between the thin portion of the reed and the face of the mouthpiece, and hence the slightest alteration in the position of the reed on the lip, and in the pressure exerted on the reed, will result in an alteration in the length of the portion of the reed which is free to vibrate. As the player ascends to the higher notes he must increase the lip pressure.

It may also be remarked that the production of the higher notes is aided by the player imagining that he is singing a high note, from which fact it must be assumed that the form of the cavity of the mouth and throat exert an influence on the production of the desired notes.

In the case of the double reed the lip pressure is also increased for the higher notes, but the change in lip pressure cannot, I submit, have such a marked effect upon the vibrating length of the reed as it had in the case of the

single reed. The double reed, as used on the oboe and bassoon, consists of two blades which are hollowed out so that when the blades are secured together there is an elliptical space between the blades. Now, in order definitely to alter the length of blade which is free to vibrate, the lips would have to squeeze the reed so hard that the blades would be pressed together. Such an action is of course impossible, since the passage of air through the reed would be stopped. The vibrating length, therefore, can be damped more or less where the lips are pressed on the reed but cannot be definitely altered. Hence it is, I think, that mere alteration of lip pressure is insufficient to produce the higher notes on wind instruments employing double reeds. In the case of single reeds, however, the lower end of the free portion of the reed adjacent the lower end of the bevel or "lay," as it is called, of the mouthpiece, may be pressed firmly against the mouthpiece so as definitely to shorten the vibrating length of the reed, and yet an air-passage will still be left between the reed and mouthpiece.

XXXI. *Ionization in the Unstriated Discharge and in the Arc.* By C. D. CHILD\*.

SO far as the writer of this article is aware, no satisfactory explanation has been given for the relation existing between the current in the unstriated discharge and the rate at which the ions recombine, nor for the relation between the electric force and the pressure of the gas. The following explanation is therefore suggested. This discussion applies also to those forms of the arc which have the same cross-section at all parts, as does the mercury arc.

*Recombination of the Positive and Negative Ions.*

A discussion of this topic was given by H. A. Wilson† a few years ago, but his fundamental equations lead to conclusions which appear at the present time to be incorrect, as is shown by the following. These equations are the ones commonly used in cases where a current is carried by ions formed in a gas, namely,

$$i = \epsilon n(u + v) \quad \text{and} \quad N = an^2,$$

where  $i$  is the current per unit cross-section,  $\epsilon$  is the charge carried by each ion,  $n$  the number of positive and also of

\* Communicated by the Author.

† Phil. Mag. [6] vi. p. 180 (1903).

negative ions per unit volume,  $u$  and  $v$  the velocities of the positive and negative ions respectively,  $N$  the number of recombinations of ions per sec. per unit volume, and  $\alpha$  some constant depending on the kind, pressure, and temperature of the gas.

In both the unstriated di-charge and in the arc the electric force is approximately independent of the current, and therefore  $u$  and  $v$  may also be considered as independent of the current, and  $\epsilon$  is a constant under all conditions. Therefore  $n$  is proportional to  $i$ . But  $N$ , the rate at which ions recombine, varies as the square of  $n$ , and therefore as the square of the current. The following considerations show that this is highly improbable.

The work which has been done in recent years on the light produced by electrical discharge indicates that part of the light, if not all, is produced by the recombination of the positive and negative ions. From this we should expect the intensity of at least part of the light to be proportional to the number of ions recombining, and if we accept the statement that the rate of recombination of the ions varies as the square of the current, we should conclude that the amount of light should vary as the square of the current. In reality the light varies approximately as the first power of the current and not as the square\*.

A consideration of the energy used to produce the ions leads us to the same result. Since the field is uniform for some distance in this form of discharge, as many ions are brought into a given region by the field as are drawn out, and hence with a constant current the number of ions formed per sec. in each c.c. must equal the number recombining. Therefore, this number must also be proportional to the square of the current, if the preceding equations are correct. It requires a certain amount of energy to produce an ion, and therefore the energy required to produce the total number of ions formed each second must also be proportional to the square of the current. However, since the electric force is constant, the total energy given to the discharge varies as the first power of the current. This brings us to the improbable conclusion that the part of the current used to ionize increases as the square of the current, while the total energy increases as the first power of this quantity.

These difficulties may be explained if we remember that there are in reality two kinds of negative ions. There are negative ions called electrons which are but small parts of molecules, having but small masses and moving with high

\* Nutting, 'Bulletin of Bureau of Standards,' iv. p. 517 (1907).

velocities, and there are negative ions formed by the union of electrons with molecules which are of molecular size and move with small velocities. The two kinds of ions have the same charges, and are equivalent to each other as far as neutralizing the electrostatic effect of the positive ions is concerned, but are very different in their velocities and consequently in their power to carry current.

As a result of this the two kinds of negative ions must be considered separately when an equation is formed for the current. This can be done by writing the equation as follows:

$$i = e(mu + n_1v_1 + n_2v_2), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $m$  is the number of the positive ions per c.c.,  $n_1$  the number of negative ions of electronic size and  $n_2$  the number of negative ions of molecular size:  $u$  is the average velocity of the positive ions,  $v_1$  the average velocity of the electrons, and  $v_2$  that of molecular negative ions.

But  $v_1$  is very much greater than  $u$  or  $v_2$ . With discharge in hydrogen the mass of a molecule is 1700 times that of an electron, and  $v_1$  is correspondingly greater than  $u$  or  $v_2$ . With discharge in mercury the mass of the molecule is 170,000 times greater than that of the electron. Consequently it would be a close approximation to write the equation as follows:

$$i = en_1v_1, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

providing that  $n_1$  is not excessively small when compared with  $m$  or  $n_2$ , and it will be shown shortly that such an assumption leads to an entirely satisfactory explanation of the observed phenomena.

That  $n_1$  is not appreciably smaller than  $m$  or  $n_2$  is shown by the high average velocity of the negative ions in the mercury arc. Stark, Retschinsky, and Schaposnikoff\* found that the average velocity of the negative ions was much greater than that of the positive. Schenkel†, from a study of the Hall effect in the mercury arc, concluded that the velocity of negative ions was  $1.42 \times 10^7$  cm. per sec. per volt more than that of the positive ions when the pressure of the gas was 1 mm.

These measurements give the average velocity of the negative ions, and if this is greater than the velocity of the positive ions, it must be that the average mass of the negative ions is much smaller than that of the positive ions. The mass of the positive ions is that of molecules, and hence the

\* *Ann. d. Phys.* xviii. p. 230 (1905).

† *Mitt. d. Phys. Ges. Zürich*, p. 13 (1906).



average mass of the negative ions is much less than that of molecules. That is, a large part of the negative ions must be electrons, and therefore  $n_1$  is not excessively small when compared with  $n_2$  or  $m$ , and equation (2) is approximately correct.

But the principal reason for assuming that this equation is correct is that such an assumption enables us to explain the difficulties which are otherwise met, for this equation leads to the conclusion that the rate at which ions recombine does not vary as the square of the current, but approximately as the first power of the current. In order to show this, one must remember that there is not only the recombination of positive and negative ions to form uncharged molecules, but that there is also the change of the negative ions from electronic to molecular size.

There are, in fact, three kinds of recombinations. First, the electrons may combine directly with positive ions and form uncharged molecules; secondly, the electrons may unite with uncharged molecules and form negative ions of molecular size which we shall call molecular negative ions; and thirdly, these molecular negative ions may unite with positive ions, forming uncharged molecules. The rate of the first of these recombinations is proportional to the number of electrons times the number of positive ions, and may be expressed by  $\alpha_1 n_1 m$ . The second rate of recombination is proportional to the number of electrons times the number of molecules, and since the number of molecules is proportional to the density of the gas, this may be expressed by  $\beta n \delta$ , where  $\delta$  is the density of the gas. The third rate is proportional to the number of molecular negative ions times the number of positive ions, and may be expressed by  $\alpha_2 n_2 m$ . In these expressions  $\alpha_1$ ,  $\alpha_2$ , and  $\beta$  are constants depending on the nature of the gas. Molecules are formed from the ions by the recombination of electrons with positive ions, and by the recombination of molecular negative ions with positive ions. Hence for the total rate at which ions recombine we may write

$$N = \alpha_1 n_1 m + \alpha_2 n_2 m; \quad . \quad . \quad . \quad . \quad (3)$$

but the rate at which the molecular negative ions recombine must equal the rate at which they are formed. Therefore,

$$\alpha_2 n_2 m = \beta n_1 \delta \quad \text{and} \quad N = \alpha_1 n_1 m + \beta n_1 \delta.$$

The chance of an electron combining with a positive ion is under all conditions much less than that of its combining with an uncharged molecule, because of the far greater number of the molecules\*. Therefore, we need consider

\* Thomson's 'Conduction of Electricity through Gases,' 2nd ed. p. 26.

only the second term in the above equation, and since  $\beta$  and  $\delta$  are independent of the current and  $n_1$  is approximately proportional to it, this term is also approximately proportional to the current, and as an approximate equation we may write

$$N = \beta n_1 \delta \propto i. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

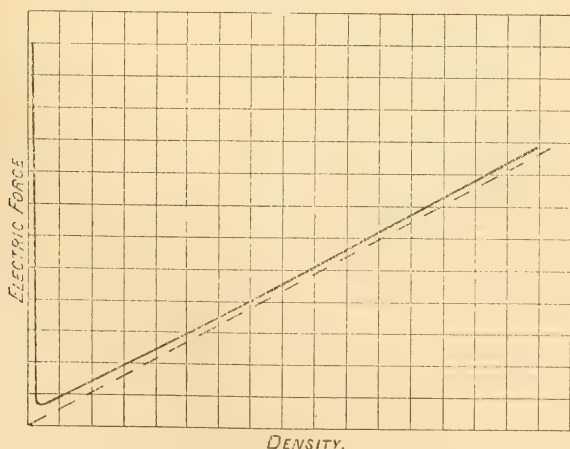
This conclusion that the rate of recombination is proportional to the first power of the current is quite in harmony with the facts to which attention has been called.

The explanation may then be summarized as follows. On account of the great velocity of the electrons approximately all of the current is carried by them. The great majority of recombinations are those of positive ions with molecular negative ions, and the rate of such recombinations varies as the number of electrons present, and consequently as the first power of the current.

*Explanation of the Relation between Electric Force,  
Density of the Gas, and Amount of Current.*

We may now go a step further and consider the relation between the electric force in the discharge and the density of the gas. It has been found that the electric force is a linear function of the density, increasing as the density increases, but that it does not approach zero when the density approaches zero. To account for this the following may be suggested. If we assume that the ionization is caused by impact, the relation between these quantities must be one

Fig. 1.



similar to that shown in fig. 1. Possibly one should add that we are also assuming that the discharge is carried by

ions, and that the positive and negative ions are continually recombining, but these statements are so universally accepted that it is hardly necessary to consider them as assumptions.

To show that some curve similar to that in the figure must hold good, let us first consider the condition when the density is large. In this case the chief obstacle to the passage of the current is the gas itself. The molecules of the gas stop the movement of the ions, so that their average velocity is small. The electrons quickly combine with molecules, since there are many molecules present; and it is difficult to produce new ions, since the mean free path of the electrons is so small that the electric force must be very large in order to give the electrons sufficient velocity to produce new ions by their impact. Clearly the electric force must increase as the density increases.

On the other hand, when the density of the gas is very small, the gas does not obstruct the movement of the ions to any appreciable extent, but there is still recombination between the negative and positive ions, and there is now great difficulty in producing new ions, due to the fact that there are few molecules to be hit by the electrons. When the number of recombinations becomes comparable with the number of collisions between molecules and electrons, a large proportion of such collisions must result in making new ions, and to cause this to occur the electric force must be large. If, for example, the number of combinations were equal to the total number of collisions between electrons and molecules, it would be necessary for each collision to result in ionization. But some of the paths of the electrons will be very short, and to meet the needs of such electrons the electric force must be very large, as shown at the left of the curve. In the limiting case it would be necessary for the electric force to be infinite.

To arrive at some idea of how the electric force varies between these two cases, we must consider the requirements necessary to maintain a current. The essential requirement is that the electric force be sufficiently large, so that new ions are produced by the impact of the electrons on the molecules as fast as they recombine. An electric force must be present also in order to move the ions after being formed, but this requirement appears to be met whenever the first one is met. If it were not, we should find that any increase in the current would require a corresponding increase in the electric force, and the force would be directly proportional to the current, as it is in metallic conduction. In reality the electric force decreases slightly whenever the current becomes

larger. In metallic conduction the number of electrons appears to be constant, and the current is determined by the electric force. In the unstriated discharge the electric force remains approximately constant, and the current is determined by the number of electrons sent into the gas from the cathode.

The number of new ions formed will depend on the number of electrons hitting the molecules, on the number of molecules to be hit, and on the velocity of the electrons. The velocity will depend on the distance through which the electron has moved since the preceding collision and on the electric force accelerating it. Only those electrons which move through comparatively large distances will be able to ionize.

Let us denote by  $V_1$  the potential difference through which an electron must pass in order to have sufficient velocity to ionize. Let  $x_1$  be the distance corresponding to such a potential difference. Then  $x_1 = \frac{V_1}{X}$ , where  $X$  is the electric force. According to the kinetic theory of gases\* the number of electrons passing through a distance as great or greater than  $x_1$  before impact will have to the whole number of impacts the ratio expressed by  $e^{-\frac{x_1}{\lambda}}$ , where  $\lambda$  is the mean free path of the electrons. Since the number of molecules is proportional to the density of the gas, we may indicate the total number of collisions per c.c. per sec. by  $bn_1\delta$ , where  $\delta$  is the density of the gas and  $b$  is a constant. The number producing ionization will then be  $bn_1\delta e^{-\frac{x_1}{\lambda}}$ , which may also be written  $bn_1\delta e^{-\frac{V_1}{\lambda X}}$ . Since  $\lambda$  is inversely proportional to the density, this may be written  $bn_1\delta e^{-\frac{c\delta}{X}}$ , where  $c$  is a constant of such value that  $c\delta = \frac{V_1}{\lambda}$ .

Some of the electrons which do not have sufficient velocity to ionize the molecules which they hit, will combine with them. It has, however, been shown by the work of Townsend† on the diffusion of ions that combinations do not always occur with such collisions. In many cases the electrons collide with molecules and again separate without any permanent effect on either the molecules or the electrons. In case of collisions between electrons and molecules there are three possible results. The electrons may ionize the

\* Meyer's 'Kinetic Theory of Gases,' p. 408; Townsend, Phil. Mag. [6] i. p. 210 (1901).

† Phil. Mag. [6] xxiii. p. 857 (1912).



molecules by their impact; the two may combine, forming molecular negative ions; or the two may separate without any permanent effect upon either.

The second of these effects would not change the total number of ions, but it would change the number of electrons, and the electrons are the principal carriers of the current. We may find an expression for the number of electrons which combine with molecules, as follows. The total number of collisions between electrons and molecules is  $bn_1\delta$ . The

number resulting in ionization is  $bn\delta e^{-\frac{c\delta}{X}}$ . Hence, the number which do not ionize is  $bn\delta(1 - e^{-\frac{c\delta}{X}})$ . If we use  $k$  to express the ratio between the number combining and the total number of collisions which do not produce ionization,

the number which combine is  $kbn_1\delta(1 - e^{-\frac{c\delta}{X}})$ . This is the same quantity as that indicated by  $\beta n_1\delta$  in a preceding paragraph.

It would be reasonable to assume that  $k$  is a function of the electric force, but it will be shown in a following paragraph that the data on the unstriated discharge agree better with the assumption that  $k$  is a constant. Therefore, for the present we shall make such an assumption.

With a steady condition of the current and a constant electric force along the length of the discharge, the number of electrons formed per second must equal the number combining with the positive electrons plus those combining with the molecules, or

$$bn_1\delta e^{-\frac{c\delta}{X}} = \alpha_1 n_1 m + kbn_1\delta(1 - e^{-\frac{c\delta}{X}}).$$

This can best be tested by expressing  $X$  in terms of  $\delta$  and  $m$ .  $\delta$  is the density and  $m$ , the number of positive ions, increases as the current increases. By the following transformations it is possible to express  $X$  in this way.

$$\left. \begin{aligned} (1+k)e^{-\frac{c\delta}{X}} &= k + \frac{\alpha_1 m}{b\delta} \\ e^{-\frac{c\delta}{X}} &= \left(k + \frac{\alpha_1 m}{b\delta}\right) \div (1+k), \\ -\frac{c\delta}{X} &= \log \left\{ \frac{k}{1+k} \left(1 + \frac{\alpha_1 m}{kb\delta}\right) \right\}, \end{aligned} \right\} \dots (5)$$

$$X = - \frac{c\delta}{\log \left\{ \frac{k}{1+k} \left(1 + \frac{\alpha_1 m}{kb\delta}\right) \right\}} = \frac{c\delta}{\log \left( \frac{1+k}{k} \right) - \log \left( 1 + \frac{\alpha_1 m}{kb\delta} \right)}. \quad (6)$$

When  $X$  and  $\delta$  are taken as the variables, this becomes the equation of a discontinuous curve, one part of which is similar in shape to that shown in fig. 1. This may be shown as follows. When the density is large  $\frac{\alpha_1 m}{k b \delta}$  approaches zero and  $\frac{X}{\delta}$  approaches  $c \div \log\left(\frac{1+k}{k}\right)$ . Since  $k$  is a constant, this quantity is a constant and the curve approaches an asymptote through the origin, which is indicated by the dotted line.

Again, when the number of combinations with positive ions equals the total number of collisions between electrons and molecules  $b n_1 \delta = \alpha_1 n_1 m$  or  $b \delta = \alpha_1 m$  and

$$\log \left\{ \frac{k}{1+k} \left( 1 + \frac{\alpha_1 m}{k b \delta} \right) \right\} = \log 1 = 0 \quad \text{and} \quad X = \frac{c \delta}{0} = \text{infinity},$$

since  $\delta$  is not zero for this value.

This corresponds to the conclusions already reached, namely, that when the density is large, the electric force increases as the density increases, and that when the number of combinations of electrons and positive ions equals the number of collisions between the electrons and molecules, the electric force must be infinite.

#### *Comparison of the Theory with the Data on Unstriated Discharge.*

Since  $c$  is equal to a constant times  $V_1$ , the value of the electric force as given in equation (6) is proportional to the potential through which an electron must go in order to ionize. It is, however, not possible to test the formula by this means; first, because we have little data about the value of  $V_1$  in different gases; and secondly, because it is not possible to change  $V_1$  without changing some of the other quantities in this formula.

When the relation between the electric force and the density of the gas is considered, we are better able to test the results of the preceding explanation.

The observations which have been made on the unstriated discharge have been made with small currents and with pressures of several millimetres. Lower pressures than these cannot in general be used without having the discharge change to the striated form. As a result, the only part of the curve shown in fig. 1 which applies to the measurements made on this form of discharge is the part at the right where  $\delta$  is large. In such cases the number of molecules is many times greater than that of the positive ions, and the number

of collisions between electrons and molecules is much greater than that between electrons and positive ions. As a result  $\frac{\alpha_1 m}{kb\delta}$  will be sufficiently small, so that the higher powers of this fraction may be neglected. When this is true,  $\log\left(1 + \frac{\alpha_1 m}{kb\delta}\right)$  is approximately equal to  $\frac{\alpha_1 m}{kb\delta}$ , and equation (6) may be written

$$X = c\delta \div \left\{ \log\left(\frac{1+k}{k}\right) - \frac{\alpha_1 m}{kb\delta} \right\}.$$

$k$  is also very small as will be shown below, so that  $\log\left(\frac{1+k}{k}\right)$  is large compared with  $\frac{\alpha_1 m}{kb\delta}$ , and we may write this equation as follows,

$$X = c\delta \left( \frac{1}{l} + \frac{\alpha_1 m}{l^2 kb\delta} \right), \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where  $l = \log\left(\frac{1+k}{k}\right)$ .

If  $k$  is a constant, this is a linear equation between  $X$  and  $\delta$ , and also between  $X$  and  $p$ , where  $p$  is the pressure, if the temperature is constant, since the pressure is then proportional to the density. This is of the form  $X = Ap + B$ . On the other hand, if  $k$  is not a constant, this is not the equation of a straight line. Measurements have been made of  $X$  and  $p$  by Herz\*, Graham†, Wiedemann and Schmidt‡, Heuse§, H. A. Wilson||, and Matthies¶, and the data in each case when plotted give a curve of the form  $X = Ap + B$ . We are therefore justified in assuming that  $k$  is a constant.

When we consider the relation between the electric force and the current, we find that the data do not agree with the equation, if we consider  $V_1$  to be a constant. In the equation,  $X$  increases when  $m$  increases, and  $m$  increases when the current increases. The increase to be expected is indeed small, but in reality there is a slight decrease when the current increases. There is but little doubt that this lack of agreement is due to the fact that  $V_1$  is not constant, but decreases slightly as the current increases. Since  $c$  varies as  $V_1$ , the expression for  $X$  decreases when  $V_1$  decreases.

\* Wied. *Ann.* liv. p. 263 (1895).

† Wied. *Ann.* lxiv. p. 58 (1898).

‡ Wied. *Ann.* lxvi. p. 320 (1898).

§ *Ann. d. Phys.* v. p. 681 (1901).

|| Phil. Mag. [5] xlix. p. 505 (1900).

¶ *Ann. d. Phys.* xviii. p. 473 (1905).

We have further evidence that  $V_1$  decreases with increasing current in the striated discharge. Thus Wehner\* found that the potential difference between consecutive striations becomes less as the current becomes greater. Again, the electric force in the arc where the current is large is very much less than it is in the unstriated discharge. Thus we may conclude that the formula agrees quite as well with the observations as is to be expected.

Equation (7) will also give some idea of the order of magnitude of  $k$ , and will confirm Townsend's statement that the collisions between electrons and molecules do not always result in combination of the two. Assuming this equation to be correct, we have

$$\frac{dX}{d\delta} = \frac{c}{l} = \frac{V_1}{\delta\lambda} \div \log\left(\frac{1+k}{k}\right), \quad \text{or} \quad \log\left(\frac{1+k}{k}\right) = \frac{V_1}{\lambda\delta \frac{dX}{d\delta}}.$$

Since  $p=c'\delta$  where  $c'$  is a constant, this equals  $\frac{V_1}{\lambda p \frac{dX}{dp}}$ .

We have some knowledge of all the quantities on the right-hand side of the last equation, but unfortunately it is not an accurate knowledge, and a slight change in any of these will produce a very large change in  $k$ . We can, however, get some idea of the value of these quantities. If we take 13.25 volts per cm. per mm. of pressure for  $dX/dp$ , which is found from the data of Herz on the discharge in hydrogen, 10.55 volts for  $V_1$ , and .0839 cm. for  $\lambda$  when  $p$  is 1 mm., as given by Davis†, the value of  $1/k$  is 13,230. That is, only one collision in 13,230 results in combination of an electron with a molecule. It is possible that this number is too large, but it does not appear altogether unreasonable, since Townsend‡ concludes from measurements on the diffusion of ions, that after 8000 collisions a large majority of the negative ions are still in the electronic state.

It would seem as if the combination of electrons and molecules might be entirely neglected, since they occur so seldom, but if this were done equation (2) would reduce to  $X=c\delta \div \log \frac{a_1 m}{b\delta}$ , in which  $X$  becomes zero when  $\delta$  becomes zero. This is contrary to the measurements which have been made on the unstriated discharge.

\* *Ann. d. Phys.* xxxii. p. 76 (1910).

† *Phys. Rev.* xxiv. p. 101 (1907).

‡ *Phil. Mag.* [6] xxi. p. 857 (1912).



*Summary.*

The amount of light given by the unstriated discharge and by the arc indicates that the rate at which ions recombine in these forms of discharge varies as the first power of the current, while the equations usually assumed for discharge through gases would lead us to expect that this rate varies as the square of the current. This is explained by assuming that approximately all of the current is carried by electrons and not by ions of molecular size, and that the great majority of the electrons combine first with molecules and afterwards with positive ions.

The fact that the electric force in this form of discharge is a linear function of the pressure of the gas is explained by assuming that the ionization is caused by the impact of the more rapidly moving electrons on the molecules, and that but few of the collisions between electrons and molecules result either in ionization or in recombination, the greater number resulting in no permanent change in either electrons or molecules.

The fact that the electric force decreases slightly when the current is increased, is explained by the added assumption that the potential difference through which an electron must go in order to ionize is smaller with larger currents than with small ones.

Colgate University,  
October, 1913.

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XXXII. *On the Relationship between the Viscosity, Density, and Temperature of Salt Solutions.* By W. J. WALKER, B.Sc., Carnegie Research Scholar, University College, Dundee\*.

[Plate IV.]

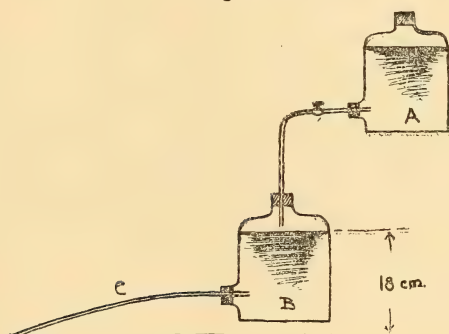
THE following notes are derived from the results of experiments carried out at the suggestion of Professor A. H. Gibson in connexion with tests on the resistance to flow of brine solutions through pipes of different diameters. The solutions were of sodium chloride and calcium chloride. The primary object of the experiments was the determination of "the kinematic coefficient of viscosity," or the ratio viscosity/density. Absolute values of the viscosity were obtained by means of the apparatus shown in fig. 1.

Reservoir A was used to maintain a constant head of about

\* Communicated by the Author.

18 cm. in vessel B. Discharge from the latter vessel took place through a glass tube C of small bore and 71.5 cm. in length. After the completion of the experiments, the diameter of the tube was ascertained by breaking it up into

Fig. 1,



pieces varying from 2 cm. to 3 cm. in length and measuring the diameters by means of a microscope furnished with micrometer eyepieces. The mean of these results gave .2590 cm. as the tube diameter. In calculating the vis-

cosities the value  $\frac{1.5V^2}{2g}$  was subtracted from the measured head.

The relationship between the percentage of salt in the solution and its density was measured by means of a Mohr specific gravity balance, with the following results in the case of sodium chloride :—

Temperature=60° F.	
Percentage Solution.	Specific Gravity.
0	1.000
6	1.042
12	1.088
18	1.134
24	1.165
28	1.198

NOTE.—Percentages reckoned as parts of salt in 100 parts of solution.

From these figures it appears that the specific gravity increases uniformly with the percentage of salt in the solution until this attains a value of about 20 per cent. After this point the rate of increase in specific gravity diminishes. This is probably due to the fact in the stronger brines, solution was not complete but that some of the material was held in suspension.

As a check on the accuracy of the viscosity apparatus, this was used to determine the viscosity of water at 62°·3 F. The mean value obtained was ·00002265 in F.P.S. units as against Poiseuille's value of ·0000227. This result gives an assurance that experiments have been carried out with a fair degree of accuracy. The results of one series of experiments on each solution are given below, the sodium chloride series being carried out at a temperature of 62°·5 F. and the calcium chloride series at a temperature of 63° F. An empirical formula was deduced for the sodium chloride series before the calcium chloride series was carried out and is given here:

$$\mu = \cdot 00002265 + \cdot 0000428(\rho - 1) + \cdot 000228(\rho - 1)^2.$$

This gives in F.P.S. units results practically identical with experimental values.

Sodium Chloride 62°·5 F.			Calcium Chloride 63° F.		
$\rho$ .	$\mu$ .	$\frac{\mu}{\rho}$	$\rho$ .	$\mu$ .	$\frac{\mu}{\rho}$
1·000	·00002265	1·000	1·000	·00002248	·993
1·008	·00002300	1·009	1·0188	·00002358	1·022
1·015	·00002335	1·016	1·054	·00002586	1·083
1·025	·00002380	1·025	1·063	·00002660	1·106
1·037	·00002445	1·041	1·084	·00002855	1·163
1·058	·00002548	1·063	1·1029	·00003020	1·210
1·065	·00002580	1·071	1·115	·00003170	1·256
1·078	·00002685	1·100	1·130	·00003318	1·295
1·095	·00002790	1·126	1·149	·00003555	1·365
1·115	·00003035	1·165	1·165	·00003800	1·425
1·142	·00003250	1·255	1·184	·00004180	1·523
1·170	·00003655	1·378	1·2078	·00005060	1·850

NOTE.— $\frac{\mu}{\rho}$  is here taken relative to water at 62°·5 F.

The curves for these solutions showing the relation between viscosity and density are given in fig. 2 (Pl. IV.).

It was intended at first to deduce an empirical formula for

the calcium chloride series, but on plotting the curves as shown, their appearance suggested an inquiry which led to the following interesting discovery of a relation between viscosity and density which does not appear hitherto to have been noticed.

In the Phil. Mag.\* Ramsay and Young published a law connecting temperatures at which different saturated vapours have the same vapour pressure. Porter, in the same magazine †, showed that if  $\frac{T}{T_0}$  be plotted against T where T and  $T_0$  are temperatures of two liquids having the same vapour pressure or the same viscosity at these temperatures, then a straight line will be obtained. From this he deduced that Ramsay and Young's law is accurately true if

$$f(p) = A - \frac{B}{T}$$

$$\text{or} \quad F(\mu) = a - \frac{b}{T}.$$

Porter showed the latter law to hold for two such dissimilar substances as mercury and water. Now in the cases given of sodium and calcium chloride it was found that if

$\frac{\mu}{\mu_0}$  be plotted against  $\mu$  where  $\mu$  and  $\mu_0$  are viscosities at similar densities, an approximate straight line was obtained, indicating the relationship

$$F(\rho) = A - \frac{B}{\mu}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In order to eliminate one of these constants this was thrown into the form

$$F'(\rho-1) = A - \frac{B}{\mu}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

When  $\rho=1$  we get  $B = \mu'A,$

where  $\mu'$  is the viscosity of water at temperature considered. (2) then becomes

$$F'(\rho-1) = A \left( 1 - \frac{\mu'}{\mu} \right).$$

\* Jan. 1886.

† June 1907 and June 1912.



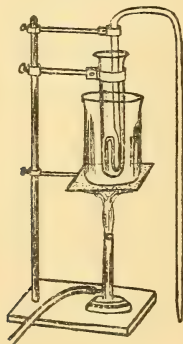
Tentatively, it was found that  $F'(\rho-1)$  was of the form  $(\rho-1)^n$  where “ $n$ ” lay between 1 and 2 for both solutions.

On plotting  $\log(\rho-1)$  against  $\log\left(1-\frac{\mu'}{\mu}\right)$  practically straight lines are obtained in each case, as shown in fig. 3.

The values for “ $n$ ” for these two lines as drawn are 1.038 and 1.055 for sodium and calcium chloride respectively.

In the Smithsonian Tables (1908) figures are given showing the relation between viscosity and density at temperatures  $10^\circ$ ,  $30^\circ$ , and  $50^\circ$  C. for sodium and calcium chloride solutions. It was thought desirable to find how “ $n$ ” and “ $A$ ” varied with temperature, so experiments were carried out at temperatures ranging from  $0^\circ$  to  $100^\circ$  C. on the sodium chloride solutions. The intermediate figures agreed well with the Smithsonian figures, except that at  $30^\circ$  C. the Smithsonian figures were slightly higher. In the case of the calcium solutions the experiments were only carried out at the lowest temperature. The apparatus was the same as used by Reynolds\* in his viscosity experiments and is shown in fig. 4. Its reliability was proved by the good results it gave

Fig. 4.



for water. The low temperatures in the experiments were obtained by means of a freezing-mixture of ice and sodium chloride. At the same time figures were obtained to show the variation of density with temperature of several solutions of different strengths. These figures are not given, but they were used to obtain for sodium chloride the curves shown in

\* Scientific Papers, vol. ii. p. 239.

figs. 5 & 6 (Pl. IV.), giving the relation between viscosity and temperature, and viscosity and density. The three upper curves in fig. 5 were for solutions of densities 1.188, 1.146, and 1.101 at a temperature of 18° C. The lowest curve is for water. In fig. 6 the curves shown are for temperatures 0°, 10°, 30°, 50°, and 100° C. Figs. 7 and 8 give the same curves for calcium chloride. Straight lines were obtained for the logarithmic values plotted as in fig. 3 for each of the above temperatures. The values of "n" for sodium chloride were found to be, when

T = 0° C.,	n = 1.48,
T = 10°,	n = 1.35,
T = 30°,	n = 1.10,
T = 50°,	n = 1.09,
T = 100°,	n = 1.075.

From these figures it appears that "n" decreases proportionally to temperature from 0° to 30° C, but from there the relative diminution becomes much less up to 100° C. Values of  $\mu$  were calculated from these values of n and were found to agree exceedingly well with the experimental values. It was desirable, however, to have a formula which would involve the three quantities  $\mu$ ,  $\rho$ , and T. The above values of "n" do not provide this, but it was found that, on assuming "n" to vary regularly in values from 1.4 to 1.0 between the limits 0° and 100° C., a quite accurate formula was obtained in the form

$$(\rho - 1)^{1.4 - .004T} = A \left( 1 - \frac{\mu'}{\mu} \right).$$

The same procedure was gone through with the calcium chloride results. The values of "n" here varied regularly from .95 to .85 as the temperature varied from 0° to 50° C. This gives as the best formula between these limits

$$(\rho - 1)^{.95 - .002T} = A \left( 1 - \frac{\mu'}{\mu} \right).$$

To obtain the value of A it is best to use the point at which the solution has its highest density. Otherwise, if A be obtained from a low density point the liability to error in calculating the viscosities at higher densities is appreciable.

The variation of A with T was next noticed. The figures below give the actual values in each case for log. A.

## Sodium Chloride.

Actual values.

At	0° C. ....	—·6795
	10° ....	—·6455
	30° ....	—·5670
	50° ....	—·4924
	100° ....	—·3016

## Calcium Chloride.

Actual values.

At	0° C. ....	—·3583
	10° ....	—·3511
	30° ....	—·3449
	50° ....	—·3333

By readjusting these values so that  $\log A$  may be regarded as a linear function of  $T$ , formulæ were obtained for each of the solutions which gave a fairly accurate relation between  $\rho$ ,  $\mu$ , and  $T$ . The readjusted values are:—

## Sodium Chloride.

Readjusted values.

At	0° C. ....	—·6790	} $\log A = -\cdot6790$ +·00374 $T$ .
	10° ....	—·6416	
	30° ....	—·5716	
	50° ....	—·4920	
	100° ....	—·3050	

## Calcium Chloride.

Readjusted values.

At	0° C. ....	—·3580	} $\log A = -\cdot3580$ +·0005 $T$ .
	10° ....	—·3530	
	30° ....	—·3430	
	50° ....	—·3330	

The tables below give a comparison between the experimental and calculated values of  $\mu$ , according to the given formulæ

$$\text{I. .... } (\rho - 1)^{1.4 - .004 T} = A \left( 1 - \frac{\mu'}{\mu} \right) \text{ for sodium chloride.}$$

$$\text{II. .... } (\rho - 1)^{.95 - .002 T} = A \left( 1 - \frac{\mu'}{\mu} \right) \text{ for calcium chloride.}$$

## I. Sodium Chloride.

T = 0°. $n = 1.4$ .			T = 10°. $n = 1.36$ .			T = 30°. $n = 1.28$ .		
$\rho$ .	$\mu_e$ .	$\mu_c$ .	$\rho$ .	$\mu_e$ .	$\mu_c$ .	$\rho$ .	$\mu_e$ .	$\mu_c$ .
1.19	187.0	187.0	1.18	128.5	127.6	1.172	74.5	73.8
1.15	150.0	150.5	1.15	111.0	110.3	1.15	68.0	67.1
1.10	122.0	123.3	1.10	91.5	91.3	1.10	57.0	56.2
1.05	107.0	107.6	1.05	79.1	79.2	1.05	50.0	48.9

T = 50°. $n = 1.2$ .			T = 100°. $n = 1.0$ .		
$\rho$ .	$\mu_e$ .	$\mu_c$ .	$\rho$ .	$\mu_e$ .	$\mu_c$ .
1.16	47.8	47.5	1.15	21.5	21.5
1.15	45.0	45.0	1.10	18.7	18.75
1.10	37.9	38.4	1.05	16.6	16.65
1.05	34.0	34.0			

## II. Calcium Chloride.

T = 0°. $n = .95$ .			T = 10°. $n = .93$ .		
$\rho$ .	$\mu_e$ .	$\mu_c$ .	$\rho$ .	$\mu_e$ .	$\mu_c$ .
1.277	310.0	308.0	1.30	273.0	277
1.200	200.0	198.0	1.20	145.5	148.0
1.10	136.0	134.5	1.10	99.0	99.8
1.05	116.0	115.5	1.05	84.0	85.2
T = 30°. $n = .89$ .			T = 50°. $n = .85$ .		
1.293	177.0	172.5	1.30	137.0	137.0
1.20	96.4	94.8	1.20	69.0	68.7
1.10	63.0	62.8	1.10	45.0	44.7
1.05	53.0	53.2	1.05	37.5	37.4

Here  $\mu_e$  = experimental value of  $\mu$ ,       $\mu_c$  = calculated value of  $\mu$ .



From these tables it appears that the greatest difference between experimental and calculated values occurs at about 30° C., but the differences (a little over 2 per cent. being the greatest) are not great when one considers the experimental difficulties involved in the measurement of viscosity.

Several other figures for different salts were taken from the Smithsonian Tables and the log. graphs plotted, and in no case was there any great deviation from the straight line. Unfortunately, however, in the majority of cases only three points are obtainable from the given figures, so that the comparison with these other solutions is not so rigid as is desirable. Again, some of the solutions actually diminish in viscosity as salt is added until a certain minimum viscosity is attained, after which the viscosity increases regularly with an increase of density as in the majority of solutions. One of the most noteworthy examples of this behaviour is found in ammonium nitrate, the density-viscosity curve of which is shown in fig. 9 (Pl. IV.). It might be thought that such a case would form a departure from the above law. It is found, however, that on giving the formula the form

$$\pm (\rho - x)^n = A \left( 1 - \frac{\mu'}{\mu} \right),$$

where  $\mu'$  is the minimum viscosity, and where the negative sign is used when  $x$  is greater than  $\rho$ ,  $x$  being the density at the minimum viscosity point, then the law does hold very approximately. Five points are given in the case of ammonium nitrate, and on plotting the log. graph for these, they were found to lie very sensibly on a straight line as shown in fig. 10. The same thing is shown in fig. 10 for manganese chloride for which four points are given in the tables, the log. graph of these also being practically a straight line. Manganese chloride, however, does not have a minimum viscosity point but behaves like the majority of salts.

The reason for the difference in the value of " $n$ " for sodium chloride as found in the two experiments \* lies, of course, in the different conditions under which these were carried out, the solutions in the first set of experiments being unfiltered.

If this law holds generally for all salt solutions, as seems probable, the best method of obtaining the formula for each salt would be to make three accurate determinations (at the same temperature) of the viscosity and density at points as far apart as possible and deduce the value of " $\log A$ " and

\* Pp. 292 & 293.

" $n$ " therefrom. This may be repeated for say another two temperatures, and thus the variation of " $\log A$ " and " $n$ " with temperature can be ascertained. The formula may then be completed.

One reason for the diminution of " $n$ " with temperature may be stated as follows. At the higher temperatures the fluidity of the solvent is increased. Now the behaviour of the solute is found to be in many ways analogous to that of a gas. This analogy would apparently become more pronounced the higher the temperature, *i. e.* the greater the fluidity of the solvent, for then the particles of solute could move about with greater freedom. The viscosity of a gas is known to be independent of density, and on glancing at figs. 6 and 8 we see that the higher the temperature the less pronounced becomes the increase of viscosity due to the increase of density. This is specially evident in the case of sodium chloride at 100° C.

It may be of interest to note here that the same method of plotting was used to determine if  $F(\mu)$  in the formula

$$F(\mu) = a - \frac{b}{T}$$

was of the form  $(\mu)^n$  in the cases of water and mercury. It was found not to be so, so that some other form must be ascribed to this function in the case of these two substances at least.

In conclusion, I desire to express my thanks to Professor Gibson for the encouragement he gave me during the course of the work.

XXXIII. *The Electrification at Liquid-Gas Surfaces.* By  
H. A. McTAGGART, M.A. Toronto; Research Student of  
Gonville and Caius College, Cambridge\*.

WHEN a liquid in the form of drops falls through a gas and splashes against an obstacle it is found to be electrified. At the same time the gas acquires a charge of the opposite sign. This charge found on the liquid varies with the liquid, the gas through which it falls, the nature of the obstacle on which it strikes, and the force of the impact. To account for this electrification it is usually supposed that at the surface of separation between the liquid and the gas, a double layer is formed, the two surfaces of which are

\* Communicated by Prof. Sir J. J. Thomson, O.M., F.R.S.

oppositely charged, and that the shock mechanically pulls these charges apart. This separation of electrifications is found to be produced by almost any kind of mechanical disturbance acting at the surface if the forces in the disturbance act quickly enough (Becker, *Jahrb. d. Rad.* ix. p. 52, 1912). The breaking away of a drop of water from a dripping tap, the bubbling of a gas through the surface of water, or the blowing of water into spray, are accompanied by disturbances of this kind. Even the sudden separation of two wetted towels which have been pressed together, will charge the towels with one sign and the air with the opposite sign.

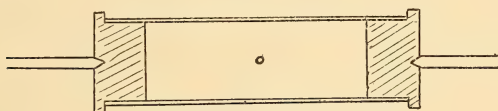
The changes that can be produced in the electrification by mechanical means are modified by the nature of the gas in contact with the liquid and by dissolved salts or other impurities which it may contain. In experiments by Professor J. J. Thomson (*Phil. Mag.* xxxvii. p. 341, 1894) the action of the gas upon the electrification produced was shown to be considerable. For example, distilled water falling through air acquired a positive charge. When it fell through hydrogen it became negatively charged, while, if allowed to fall through its own vapour, it acquired no charge. Small quantities of salts dissolved in the water produced very remarkable effects on the electrification. The most active in this respect were some of the organic salts which are known to be readily adsorbed into the surface (Freundlich, *Kapillarch.* p. 248). This fact has suggested that the electrical double layer may be a result of adsorption.

It might be expected that the nature of this double layer, if it actually exists, would be influenced not only by the liquid and the salts dissolved in it, but to some extent also by the gas. At liquid-solid surfaces the electrification is not determined by the solution alone. The solid plays an important part—as experiments in cataphoresis and electric endosmose clearly show—but the way in which the solid (or gas) affects the charge in the double layer is not apparent. Nor is it clear how the ions of the dissolved salts, or those of the liquid itself, enter into the formation of the layer. To add to the information on these points is the object of this paper, which describes some experiments on liquid-gas surfaces.

In 1861 Quincke observed (*Pogg. Ann.* cxiii. p. 513, 1861) that in water through which an electric current was passing, small bubbles of air moved toward the anode, while in turpentine they moved toward the cathode. This motion

must be due to the presence of an electric charge upon the surface of the bubble, and its velocity will then be a measure of the charge. An examination of these velocities will thus provide some further data regarding the electrification at liquid-gas surfaces. In his experiments Quincke used glass tubes of small bore (0.4 to 2 mm. diam.) in which to observe the motion of the bubbles. One disadvantage in such small tubes is the disturbing effect of the endosmose currents, besides which there is the difficulty of keeping the bubble from sticking to the wall. Instead of this it is possible to use a glass tube rotating about its axis as shown in fig. 1.

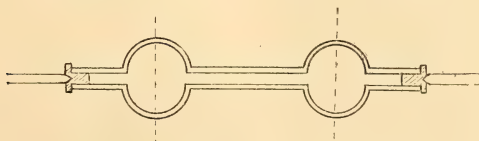
Fig. 1.



The ends are closed by metal electrodes which are counter-sunk to receive the pivot points upon which the tube rotates. When the tube is in motion the current is led in through the liquid by means of the pivot supports. A bubble of gas in the rotating liquid takes up a position on the axis if the bubble is fairly small and if the speed of rotation is high enough. The motion of the sphere of gas along the axis due to an applied electric field may then be examined. This is the method employed in this paper.

To reproduce the effects observed by Quincke a preliminary trial was made with a rotating cell of the form shown in fig. 2.

Fig. 2.



It consists of a piece of capillary tubing near the ends of which two bulbs are blown. The inner surface from the ends up to the dotted lines was silvered in order to provide electrodes as large as possible. A small hole was left in one of the bulbs through which a bubble of gas could be introduced. This could be done very easily when the tube was at



rest by using a fine tube fitted with a screw as shown in fig. 3.

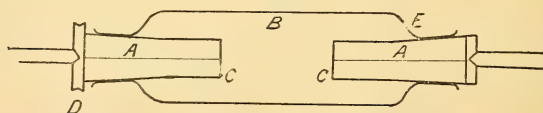
Fig. 3.



It is made by drawing down an ordinary piece of glass tubing to a fine capillary and fastening a plate with a screw through its centre to the large end. When this apparatus is filled with water, if the screw be turned back the water retreats along the capillary followed by air, any quantity of which may then be expelled into the cell by turning the screw forward again. The cell was set in motion by a small electric motor connected to it by a belt of fine thread running over pulleys. This apparatus gave, even when set up in a more or less careless way, a very interesting exhibition of the bubble moving along the axis, now fast, now slow, as the potential between the ends was altered.

The velocity of a bubble of gas in such a cell is not, however, its real velocity through the liquid. In tubes of such small bore the endosmose sets up a current along the wall which returns along the axis, increasing or diminishing the true velocity according to circumstances. Another error, due to currents in the liquid, is introduced if the speed of rotation is not uniform, an error which it is almost impossible to avoid with an ordinary type of motor. In making actual measurements a cell of the form shown in fig. 4 was used.

Fig. 4.



The glass stoppers AA with platinum electrodes on their ends *cc* are ground into the tube B and furnished with metal bearings to run on the pivot points. A wire running through the stoppers connects the electrodes with the bearings. Bubbles of gas are introduced through a small hole at E. To ensure uniform rotation a Rayleigh motor (*Scientific Papers*, Lord Rayleigh, vol. ii. art. 56, p. 355) was used which drove a belt of thread over the pulley D. This worked fairly well if the thread was kept moistened with oil to

prevent it slipping. The drifting of the bubble due to gravity was controlled by levelling-screws in the base of the apparatus. It was found that when all adjustments were made, the bubble, observed through a low-power microscope, would remain on the hair-line for some time.

With this cell an examination was made of (1) the effect of the size of the bubble on its velocity, (2) the relation between the velocity and the potential gradient, (3) the value of the velocity in distilled water of conductivity about  $5 \cdot 10^{-6}$ . The velocity was measured by noting the time—with a stop-watch—taken by the bubble to move over a fixed number of scale-divisions in the microscope. By a simple device the watch was started (or stopped) and the electric field applied (or removed) simultaneously. To eliminate a possible error due to the tube not being exactly level, the bubble was made to move a definite distance in one direction and to retrace it in the opposite direction. The diameter of the bubble was measured on the microscope-scale as the tube was rotating. The following readings on bubbles of air of various sizes show the accuracy obtained. In the first column is the diameter in mm. ; in the second, five successive readings of the time required to move over 20 scale-divisions (45 divisions = 1 mm.). Since the field between the electrodes was not uniform, the readings were taken at a fixed distance from one electrode.

Diam.	Time in secs.					Average.
·06	$9\frac{1}{2}$ ,	$10\frac{1}{5}$ ,	$10\frac{1}{5}$ ,			10·1
·08	10 ,	$10\frac{1}{5}$ ,	$10\frac{1}{4}$ ,	$10\frac{3}{4}$ ,	$9\frac{3}{4}$	10·2
·10	10 ,	$10\frac{1}{4}$ ,	$10\frac{1}{4}$ ,	$10\frac{1}{5}$ ,	$10\frac{3}{4}$	10·3
·12	$10\frac{3}{4}$ ,	$10\frac{1}{4}$ ,	$10\frac{1}{4}$ ,	$10\frac{1}{5}$ ,	11	10·5
·14	10 ,	10 ,	10 ,	$10\frac{1}{4}$ ,	10	10·0
·16	10 ,	10 ,	10 ,	10 ,	10	10·0
·16	$10\frac{3}{4}$ ,	11 ,	11 ,	11 ,	$10\frac{3}{4}$	10·9

If the difficulty of maintaining a uniform speed of rotation were fully overcome, the average time for bubbles of different sizes would probably be the same. Bubbles larger than ·2 mm. gave inconsistent results, due apparently to eddy currents set up by their failure to remain exactly on the axis. Very small bubbles, formed sometimes by the gradual absorption of the gas by the water, were observed to leave the axis in an irregular way as if their buoyancy were no longer sufficient to keep them on the axis. It may be concluded then, that, within the limits given in the table above, the velocity is independent of the size.

The velocity is proportional to the potential gradient, at least for differences of potential that are not very small. Measurements of velocities in fields of less than 6 volts per cm. were not made. The following table gives the time taken by a bubble in moving 40 divisions under a field of 16 volts and of 8 volts. Readings were taken at six points equally spaced between the electrodes to observe at the same time the variation in the field. Near the electrodes the times are shortest, *i. e.* the velocity is greatest.

	1.	2.	3.	4.	5.	6.
16 volts .....	$8\frac{1}{4}$ $8\frac{1}{2}$	$10\frac{3}{4}$ 10	12 $11\frac{3}{4}$	$11\frac{1}{2}$ 12	$10\frac{1}{4}$ $10\frac{1}{2}$	$8\frac{3}{4}$ $8\frac{1}{2}$
Average .....	8.3	10.3	11.8	11.7	10.3	8.6
8 volts .....	18 16	21 20	25 23	26 23	24 $20\frac{3}{4}$	20 17
Average .....	17	20.5	24	24.5	22.3	18.5

When the voltage is doubled the time is halved, *i. e.* the velocity is doubled.

To get an estimate of the actual velocity per unit fall of potential, it is necessary to know the average value of the velocity. This may be got by plotting a curve with the distances of a point on the axis from the electrode as abscissæ, and as ordinates the velocities or times to move over a given distance about the point, and finding the average ordinate for the curve. The value obtained for one set of readings was 9.4 sec. which was the average time taken to move 20 divisions of the scale each way or 40 in all. The fall of potential was 22.8 volts per cm. This gives a velocity in cm./sec./volt/cm. of

$$\frac{40}{45 \cdot 10} \cdot \frac{1}{9.4} \cdot \frac{1}{22.8} = 4.1 \cdot 10^{-4}.$$

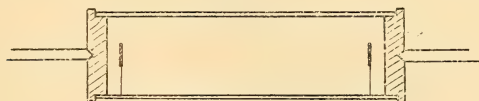
An average of four sets of readings at another time gave  $3.9 \cdot 10^{-4}$ . It may be concluded then that the velocity of small spheres of air in water of this purity is about  $4 \cdot 10^{-4}$  cm./sec./volt/cm.

No effort was made to prepare water of extreme purity, but rather to obtain by a fixed method of distillation water of fairly constant quality. It invariably contained air and carbon dioxide, to some extent. Under these conditions spheres of hydrogen, oxygen, and illuminating gas all had

practically the same velocity as air. For hydrogen an average of three sets of readings gave  $4.2 \cdot 10^{-4}$ ; of three others  $4.1 \cdot 10^{-4}$ . From Professor Thomson's experiments on the electrification of drops one might expect to find a difference in the velocity of hydrogen and oxygen. In his experiments the water was carefully freed from dissolved gases and a perfectly fresh surface was exposed with each drop, conditions difficult to obtain in a rotating cell. However, water thoroughly boiled was tried but no change of sign occurred with hydrogen as compared with oxygen, and, as far as could be observed, there was no difference in velocity. No actual measurements were made on account of the rapidity with which the bubble was absorbed by the water.

Experiments were then made to study the influence of small amounts of dissolved electrolytes upon the surface electrification. For this purpose a slightly different form of cell was used, designed to allow the use of larger currents than were possible in the last cell. A straight piece of glass tubing 2.3 cm. in diameter and about 7 cm. long was fitted with brass stoppers covered on one face with platinum to act as electrodes (fig. 5).

Fig. 5.



Two thin disks of glass mounted just in front of the electrodes prevented small bubbles of gas which might form on these from drifting out into the liquid and disturbing the bubble under observation. For the very dilute solutions that were used this cell was found to be fairly suitable. It was filled and emptied through a small hole in the end. Mathematically (Lamb, Brit. Assoc. Report, 1887, p. 495), in such a closed cylinder the endosmose along the walls would set up a return current along the axis. In a tube of this size, however, it would be negligible, giving an error of the same order as that present in U-tube methods of determining the velocities of colloidal suspensions.

A considerable amount of work has been done on liquid-solid surfaces and on the effects of dissolved electrolytes on the surface electrification. Hardy (Journ. Phys. Chem. iv. p. 235, 1900) gives as a general rule that, in the case of colloids, the coagulative power of a salt is determined by the



valency of one of its ions. That ion which is of the opposite electrical sign to the colloidal particle is the one which causes the coagulation, *i. e.* it is the ion which annuls the charge on the colloid. In endosmose experiments with porous diaphragms, Perrin (*Journ. de Chim. & Phys.*, ii. 1904, iii. 1905) finds a similar rule to hold regarding the activity of an ion in discharging the solid-liquid surface. A trivalent ion is much more active in this respect than a monovalent ion. A positive ion reduces the charge on a negatively charged surface and conversely. In general, at a liquid-solid surface, the solid is charged negatively in a basic solution, and positively in an acid solution. It will be seen that these rules apply, in a general way, to liquid-gas surfaces as well.

The two acids HCl and HNO<sub>3</sub>, having the monovalent positively charged hydrogen ion, were tried in very dilute solutions. With increasing concentration the negative charge on a bubble of air was reduced until it was practically neutralized. Very strong solutions could not be used because of the disturbing effect of gases given off at the electrodes. In the highest concentration that was used, however, no reversal of the sign was found. HCl was used in concentrations from 10<sup>-7</sup> equivalents per c.c. to 10<sup>-5</sup> equivalents per c.c. as estimated against standard baryta-water. HNO<sub>3</sub> over a similar range of concentrations gave practically the same results as HCl.

To obtain, if possible, some examples of a reversal of the sign of the charge, a number of trivalent positive ions were chosen. Readings for three nitrates are given in the tables below. In the first column are the concentrations in equivalents per c.c., in the second the time taken by a bubble of air in moving over a fixed distance, and in the third the sign of its charge. When the velocities are too slow to be timed conveniently the words "slow," "faster," are used to give a general idea of the motion.

La(NO <sub>3</sub> ) <sub>3</sub> 6 H <sub>2</sub> O.	Time.	Charge.
	Seconds.	
10 <sup>-9</sup> . 7.5	40	-
10 <sup>-8</sup> . 7.5	64	-
10 <sup>-7</sup> . 3.7	240	-
10 <sup>-7</sup> . 7.5	—	0
10 <sup>-6</sup> . 3.7	slow	+

Al(NO <sub>3</sub> ) <sub>3</sub> 16 H <sub>2</sub> O.	Time.	Charge.
	Seconds.	
10 <sup>-9</sup> .4	40	—
10 <sup>-9</sup> .8	67	—
10 <sup>-8</sup> .24	slow	+
10 <sup>-8</sup> .4	„	+
10 <sup>-7</sup> .4	faster	+
10 <sup>-6</sup> .2	„	+

Cr(NO <sub>3</sub> ) <sub>3</sub> 18 H <sub>2</sub> O.	Time.	Charge.
	Seconds.	
10 <sup>-9</sup> .4	20	—
10 <sup>-8</sup> .2	28	—
10 <sup>-8</sup> .4	34	—
10 <sup>-7</sup> .1.2	50	—
10 <sup>-7</sup> .4	80	—
10 <sup>-7</sup> .8	slow	—

The first two salts reverse the sign of the charge on a water-air surface, and it seems likely that the chromium salt would have done the same if the concentration could have been made a little greater.

The following tetravalent nitrates were then tried :—

Th(NO <sub>3</sub> ) <sub>4</sub> 12 H <sub>2</sub> O.	Time.	Charge.
	Seconds.	
10 <sup>-11</sup> .7	26	—
10 <sup>-10</sup> .7	77	+
10 <sup>-9</sup> .7	57	+
10 <sup>-8</sup> .1.4	48	+
10 <sup>-8</sup> .2.8	40	+

Zr (NO <sub>3</sub> ) <sub>4</sub> .	Time.	Charge.
	Seconds.	
10 <sup>-9</sup> .5	23	—
10 <sup>-8</sup>	—	0
10 <sup>-8</sup> .5	95	+
10 <sup>-7</sup>	35	+
10 <sup>-7</sup> .5	30	+

The positive ions Th and Zr not only neutralize the negative charge but they give the surface a large positive charge. The thorium salt is the most remarkably active in this respect of all the salts used.

Two tetravalent chlorides were tried but they showed very slight effects :—

PtCl <sub>4</sub> 5 H <sub>2</sub> O.	Time.	Charge.
	Seconds.	
10 <sup>-9</sup>	16	—
10 <sup>-7</sup>	17	—
10 <sup>-6</sup>	26	—
10 <sup>-6</sup> .2	40	—

SnCl <sub>4</sub> 8 H <sub>2</sub> O.	Time.	Charge.
	Seconds.	
10 <sup>-9</sup> .7	19	—
10 <sup>-8</sup> .3.5	28	—
10 <sup>-8</sup> .7	32	—
10 <sup>-7</sup> .1.4	25	—

In these cases it is likely that the metal forms part of a complex ion, and is therefore not free to exhibit the full effect of its valency (Whetham, 'Theory of Solutions,' p. 196).

Hexavalent chromium in CrO<sub>3</sub> gave results of a similar kind :—

$\text{CrO}_3$ .	Time.	Charge.
	Seconds.	
$10^{-8}$	20	—
$10^{-7}$	25	—
$10^{-7}, 5$	30	—
$10^{-6}$	50	—
$10^{-6}, 2$	?	—

The effect of negative ions on positively charged bubbles was then examined. For this purpose the trivalent and tetravalent ion ( $\text{FeCy}_6$ ) in potassium ferri- and ferrocyanide were used. To obtain a positively charged bubble to begin with, a solution containing  $10^{-8}$  equivs./cc. of thorium nitrate was made. In this a bubble of air has a small positive charge. The following tables show the effect on this positive charge of the negative ions in different concentrations.

$\text{K}_3\text{FeCy}_6$ .	Time.	Charge.
	Seconds.	
0	slow	+
$10^{-8}$	"	+
$10^{-8}, 5$	"	almost zero.
$10^{-7}$	—	0
$10^{-7}, 2$	slow	—
$10^{-7}, 3$	40	—

$\text{K}_4\text{FeCy}_6 \cdot 3\text{H}_2\text{O}$ .	Time.	Charge.
	Seconds.	
0	slow	+
$10^{-9}, 2$	"	+
$10^{-9}, 4$	43	—
$10^{-9}, 8$	30	—
$10^{-8}$	20	—
$10^{-8}, 3$	28	—
$10^{-7}$	37	—



The tetravalent salt neutralizes the positive charge at a much smaller concentration than the trivalent.

The monovalent positive ion H, and negative ion OH in HCl and KOH respectively were tried in water made electrically neutral by adding a very small quantity of  $\text{Al}(\text{NO}_3)_3$ . When HCl was added to this solution the bubble became positively charged. When KOH was added it gave the bubble a negative charge.

In ordinary distilled water bubbles of hydrogen and oxygen have practically the same velocity. There is probably a difference which, however, cannot be detected with certainty under the conditions of the experiment. This difference might show itself more definitely in a solution almost electrically neutral. The following readings with air, hydrogen, and oxygen were taken to see if a difference could be observed:—

$\text{Al}_2(\text{SO}_4)_3$ .	Air.	O.	H.
$10^{-9}.2$	—	—	—
$10^{-9}.3$	0	—	+
$10^{-9}.5$	+	—	+
$10^{-8}$	+	0	+
$10^{-7}$	+	+	+

It appears that the hydrogen changes sign at a smaller concentration than the oxygen, so that in this case, at least, the surface electrification is not independent of the gas.

The following unexpected effect was observed when water was used which had been boiled to free it from air. The water was made almost but not quite electrically neutral by adding  $\text{Th}(\text{NO}_3)_4$ , and a bubble, placed in this solution, was observed under the microscope. In this partially air-free solution, the bubble was gradually absorbed by the liquid and finally disappeared, but its electric charge during this process did not remain the same. At first it was negatively charged. As it diminished in size the negative charge gradually disappeared until the bubble was neutral. As it continued to diminish in size it began to acquire a positive charge which slowly increased till the bubble became too small to examine. This effect will be referred to again.

*Discussion.*

Small spheres of gas electrically charged in water move in an electric field with a velocity of the same order as the velocity of colloidal particles. The motion of these particles is regarded as due to a continuous relative displacement in opposite directions of the two faces of a double layer, one of which is fixed to the solid particle. The velocity of such a particle is given by Lamb's formula (B. A. Report, p. 495, 1887)

$$u = \frac{H\rho\delta}{\mu},$$

where  $u$  = vel. of particle,  $\rho$  = surf. density of charge,  
 $H$  = pot. grad.,  $\delta$  = thickness of layer,  
 $\mu$  = viscosity of liquid.

This equation will apply to the motion of spheres of gas in a liquid if a double layer exists at the liquid-gas interface. That surface of the double layer which touches the gas would not be attached to a solid surface as in the case of a colloidal particle, but it might be regarded as forming a sort of flexible shell filled with the gas.

There is no doubt that a film of some rigidity is formed about the gas, which acts toward the contiguous liquid like a solid surface so far as endosmose effects are concerned. Hardy (Proc. Roy. Soc. B. lxxxiv. 1911) has examined with some care the case of a plane air-water surface. An electric current was observed to drive small particles of graphite immersed just under the film past the surface with the same velocity as particles near the solid walls of the containing vessel. Small particles resting upon the film did not move appreciably. A sphere of gas in liquid is enclosed in a film of this sort which forms one surface of the double layer and preserves its identity, more or less, as it moves through the liquid. We may, then, with some reason assume Lamb's formula to be applicable and employ it to find the charge on a bubble of air in water.

We have in E.S. units :—

$$\begin{aligned}\rho &= \frac{\mu u}{H\delta} \\ &= \frac{0.01 \cdot 4 \cdot 10^{-4}}{300 \cdot 10^{-8}},\end{aligned}$$

putting the viscosity at 0.01 and the thickness at  $10^{-8}$  cm.,

$$\begin{aligned}\text{or} \quad &= \frac{0.01 \cdot 4 \cdot 10^{-4}}{300 \cdot 10^{-8} \cdot 3 \cdot 10^9} \text{ coulombs} \\ &= 4 \cdot 10^{-5} \text{ nearly.}\end{aligned}$$

The charge on a sphere of any size may be found by multiplying this density by the surface area. The following table compares with this the amount of electrification set free (1) by a drop in a waterfall experiment, (2) by a drop broken up in a current of air (Simpson, Phil. Trans. A. 209. p. 379, 1909), and (3) by the breaking off of a drop from a source (see Becker, *loc. cit.*).

Experiment.	Diam. of sphere.	Charge calc. in coulombs.
Cataphoresis .....	7.8 mm.	$7.6 \cdot 10^{-5}$
	4.4 „	$2.4 \cdot 10^{-5}$
Waterfall exp. ....	7.8 „	$2.8 \cdot 10^{-12}$
	4.4 „	$0.89 \cdot 10^{-12}$
Drops broken up by a current of air .....	7.8 „	$1.7 \cdot 10^{-12}$
Breaking off of a drop...	4.4 „	$5.28 \cdot 10^{-14}$

If the estimates made in these various cases are not too wide of the mark, it is evident that only a very small fraction of the charge is set free by such mechanical disturbances as those mentioned.

The difference of potential (V) between the surfaces of the double layer may be calculated from

$$\frac{\mu u}{H\delta} = \rho = \frac{KV}{4\pi\delta}, \text{ i.e. } V = \frac{4\pi\mu u}{HK},$$

if the thickness of the layer be small in comparison with the radius of the sphere.

In E.S. units

$$V = \frac{4.3 \cdot 14.0 \cdot 01.4 \cdot 10^{-4}}{300.81},$$

or in volts

$$\begin{aligned} &= \frac{4.3 \cdot 14.0 \cdot 01.4 \cdot 10^{-4} \cdot 300}{300.81}, \\ &= \underline{0.055}. \end{aligned}$$

In a consideration of the electrical effects observed at liquid-gas surfaces, differences must be noted between the conditions of experiments like waterfall experiments, bubbling of gas through water, or spraying experiments and cataphoresis experiments like those described in this paper. The surface-density of electrification need not be the same in the two cases. In solutions the concentration of the salt in the surface does not reach an equilibrium value the moment the surface is formed. For this reason, the electric density will

have a value in a freshly formed surface different from its value in an older surface. One may refer to the two types of experiment as the dynamical and statical, in the same way that one refers to corresponding methods of measuring surface-tensions of solutions. Not only is there a gradual adsorption of salt into the surface on the liquid side, but there may be an adsorption of gas on the opposite side. In a dynamical experiment the surface will not be in that equilibrium state which exists in a statical one.

Again, it is possible that the gas does not play the same part in producing the electrification in the two cases. For example, it is not improbable that a sphere of water-vapour in water would be found to be charged in the statical experiment, while a drop of water falling through its own vapour is known to give no electrical effect. In the static case H and O show very slight differences in charge, but in dynamic experiments they give rise to charges of opposite sign. The fact that so many substances in contact with water are negatively charged indicates that water by itself produces an electrification upon which is superposed an electrification due to the substance in contact with it. It is probable that in the static experiment the hydrogen and oxygen exert a very small influence on the charge observed, but in dynamic experiments they play an important part. When these gases are torn away from the water by the mechanical forces, the violence of the separation may give rise to an electrification which is not apparent in the statical observations and which depends as to its sign and amount upon the nature of the gas.

The changes in the electrification produced by dissolved salts are not easy to explain, the difficulty being increased by a lack of knowledge of the nature of the ions formed and the amount of hydrolysis which occurs. Where there is complete dissociation—as in the dilute solutions here used—the ions formed would tend to charge the surface with their own sign. This tendency, however, is stronger in some ions than in others, and the same ion does not exhibit the same power to charge different surfaces. The H-ion, for example, shows quite different powers of precipitation toward colloidal  $As_2S_3$ , gold-sol, mastic and egg-white (Mines, *Koll.-Chem. Beih.* iii. p. 193, 1911-12). In the case of liquid-gas surfaces the H-ion does not seem to show a very strong charging power, as indicated by the acids HCl and  $HNO_3$ .

Of the three trivalent nitrates of La, Al, Cr, the first shows scarcely any hydrolysis (Perrin, *loc. cit.*), and one might expect the effects observed to be due to the simple ions La



and  $\text{NO}_3$ . In the other two cases hydrolysis produce a supply of H-ions, to which the higher activity of the Al-salt may be ascribed. One would expect the Cr-salt for the same reason to be more active than La, but its effect is even less. Similar discrepancies occur in the stability of these metals in colloidal form (Biltz, *Berl. Ber.* xxxv. p. 4434), and no satisfactory explanation seems possible at present.

Of the two tetravalent nitrates Th and Zr the first is unusually active, the merest trace of the salt being sufficient to reverse the charge. Both salts hydrolyse and their colloidal hydroxides are prepared by dialysis. Thorium is remarkable also for its stability as a colloid, being much more stable in the presence of added electrolytes than Zr (Biltz, *loc. cit.*). In endosmose experiments using water against glass and quartz, Elissaffoff (*Zeit. Phys. Chem.* lxxix. p. 385, 1912) finds that  $\text{Th}(\text{NO}_3)_4$  has the same high charging power. This activity cannot be due to the presence of H-ions resulting from hydrolysis altogether, because the conductivity of the solution is relatively small. It has a large atomic weight, a fact worth noting in connexion with similar observations on the activity of heavy metals in endosmose experiments.

The chlorides of platinum and tin and the oxide of chromium evidently produce ions whose charges are small. Simple ions are not formed in these cases—a necessary condition apparently for the production of the greatest effect on the surface electrification.

The two negative ions,  $\text{FeCy}_6^{\cdots}$  and  $\text{FeCy}_6^{\cdots\cdots}$ , follow the valency rule that the ion with a larger charge is more active than one with a smaller charge. Similar results for positively charged copper in colloidal solution have been obtained by Burton (*Phil. Mag.* vol. xvii. no. 100, April 1909) who found the charge to be reversed by  $\text{K}_3\text{PO}_4$  and  $\text{K}_3(\text{FeCy}_6)$ .

In a general way the valency determines the charging power of an ion, but it is not the only factor apparently which has an influence. The greater activity of the ions of the heavy metals has been mentioned. The complexity of the ion also is associated with peculiarities in its activity. Mines (*loc. cit.*) has examined the action on colloidal substances of the complex trivalent ion  $[\text{Co}(\text{NH}_3)_6]$  in Luteo-cobalt chloride and of simple trivalent ions. Some colloids are sensitive to both complex and simple ions, and some only to simple ones. An emulsion of olive-oil in water differentiates between the two, the simple ion being 170 times more powerful in precipitating the oil.

From these experiments with a rotating cell, it would seem

that in the static type of experiment the charge at a water-gas surface is very slightly affected by the nature of the gas. Let us suppose for simplicity that the gas has no effect and that—following Prof. J. J. Thomson's view—the liquid in the surface layer is chemically unsaturated. The adsorbed gas, oxygen or hydrogen for example, would become attached to water molecules, but in such a way as not to affect the value of the charge in the electrical double layer, which would have the same sign and value as if the gas were absent. When, as in a waterfall experiment, a separation of the gas and water molecules occurs, the electrons are shared between them in a different way. Oxygen, having an affinity for negative electrons, will carry away an excess of them, giving the gas a negative charge. Hydrogen will leave an electron behind in the water and go off positively charged. In other words, the dynamical experiment brings out the difference in the chemical, *i.e.* the electrical, nature of the gas.

This simple view may be slightly modified in an actual case. Oxygen might attract negative ions into the surface and give it a larger negative charge than hydrogen would, as is shown, for example, in the comparison readings for these two gases in  $\text{Al}_2(\text{SO}_4)_3$ . In the static experiments the ions in the liquid will determine the surface charge, and since in water a surface is always negative, one may suppose the existence of a selective adsorption of  $\text{OH}$  ions. In support of this is the fact that the surface is electrically neutral when  $\text{H}^+$  ions are in excess, as in acid solutions (leaving polyvalent ions out of consideration). When dissolved salts are present, their adsorption modifies the charge again, but the gas in contact still shows scarcely any effect. This neutrality was observed by Metcalf (*Zeit. Phys. Chem.* lii. p. 1, 1905) on the formation of films or crusts upon water by methyl violet, peptone, &c. He could detect no difference in the films when oxygen or hydrogen was in contact with them. A similar behaviour is observed in the change of sign which occurs when a bubble of hydrogen or oxygen is slowly absorbed into a solution of thorium nitrate as described above. When first introduced into the liquid the bubble is negatively charged. As it diminishes in size it gradually becomes neutral and then slowly takes on a positive charge. The effects are exactly those that would be produced if the concentration of the salt were slowly increased, as shown in the table above for thorium nitrate. It is natural to conclude

that a progressive change in the concentration at the surface takes place as the bubble gets smaller. The surface layer first formed adsorbs a certain amount of salt which it apparently retains as it gets smaller, thus increasing the concentration. As in Metcalf's experiments no difference could be observed between the action of hydrogen and oxygen in this case.

This view of the action of the gas in these experiments is merely an hypothesis, and the work is being continued with the object of finding out more accurately the part played by the gas and by the salts dissolved in the liquid.

### *Summary.*

A rotating cell method of examining the electric charge on small spheres of gas in a liquid has been worked out.

Quincke's observations on the movement to the positive pole of small spheres of air, oxygen, and hydrogen in distilled water were repeated, using the rotating cell.

The velocity of small spheres of gas in water was found to be proportional to the potential gradient and independent of their size (within limits).

The velocity of spheres of air, oxygen, and hydrogen in water was found to be about  $4 \cdot 10^{-4}$  cm./sec./volt/cm.

Dissolved salts affect the charge at a gas-liquid surface, the activity of the salt depending on the charge carried by its ions in solution.

An air-water surface—in the absence of polyvalent ions—is electrically neutral in a slightly acid solution.

A sphere of gas in a solution can change the sign of its charge as it diminishes in size, by being absorbed into the solution.

Under the conditions of these experiments the electric charge at a liquid-gas surface appears to be almost independent of the nature of the gas.

My best thanks are due to Professor Sir J. J. Thomson for suggesting this research and for his kind advice during the progress of the work.

XXXIV. *The Theory of X-Ray Reflexion.* By C. G. DARWIN, M.A., *Lecturer in Mathematical Physics in the University of Manchester*.\*

1. **T**HE formulæ developed by Prof. Laue† in connexion with the interference of X rays in crystals are competent to show the positions in which the interference maxima occur, but do not give the intensities at the maxima. For it is readily calculated that it is impossible experimentally to get a crystal so small that the spherical waves coming from a source at any manageable distance can be regarded as plane. If, following Bragg‡, we regard the phenomenon as due to reflexion in a set of parallel planes of atoms, the extreme shortness of the waves makes the Fresnel zones in these planes very small (in Friedrich and Knipping's§ experiments they would be about  $2 \times 10^{-7}$  sq. cm.), and this vitiates the application of Laue's formula for the intensity. In a later paper Laue|| has made use of the Fresnel diffraction principles to account for the shapes of the spots on the interference photographs, but a complete theory must regard the whole problem as one of spherical waves.

In working out such a theory there is great advantage in taking as model that experimental arrangement which has in fact proved most fruitful, reflexion from the planes parallel to an external face of a crystal. This gets rid, both for theory and experiment, of a great deal of rather complicated geometry, which is useful in investigating the structure of crystals, but has nothing to do with the nature of the reflexion.

## 2. Assumptions.

We shall assume simply that X-ray phenomena are a branch of optics. The optical theories of diffraction, and also of dispersion, etc., work out correctly on principles depending on a simple vibration theory, although some of the phenomena of light can only be reconciled with this theory with difficulty. Thus the photoelectric effect depends on Planckian considerations which seem contradictory to the wave theory. In the same way we shall suppose that X rays obey the ordinary laws of the electromagnetic theory, in

\* Communicated by Sir Ernest Rutherford, F.R.S.

† M. Laue, *Kön. Bay. Ak.* 1912, p. 303.

‡ W. L. Bragg, *Proc. Camb. Phil. Soc.* vol. xvii. i. p. 43.

§ W. Friedrich & P. Knipping, *Kön. Bay. Ak.* 1912, p. 311.

|| M. Laue, *Annal. d. Phys.* Bd. xli. p. 1003 (1913).



spite of the well-known fact that their absorption occurs by means of the emission of high-speed electrons. But a somewhat less satisfactory assumption must also be made. The observed exponential absorption of homogeneous rays is probably a statistical effect, but it is here assumed that the *amplitude* of a wave passing through matter diminishes exponentially with an absorption coefficient half that observed for the intensity. This assumption brings out the correct form for the absorption, and is to a certain extent justified by one of the experiments of Mr. Moseley with the present writer\*. It was found that the intensity of reflexion from a crystal was cut down by exactly the same amount by a given piece of aluminium, whether it was placed so as to intercept the whole radiation before reflexion, or the selected radiation after reflexion. This experiment proves that the absorption of a heterogeneous beam can be calculated by Fourier analysis.

It should be said at once that part of the quantitative discussion in the present paper is inadequate and can only be regarded as a first approximation, but several points of interest have emerged. It is hoped to treat of a more complete theory in a future paper.

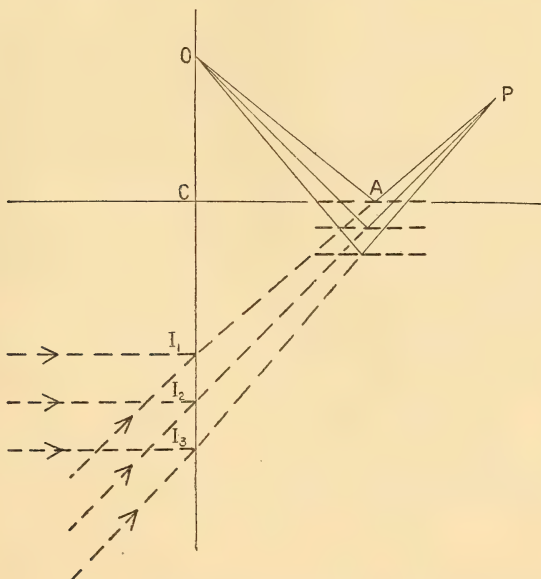
### 3. *The Structure of a Reflected Line.*

The first point we shall consider is employed in Moseley's† method for discovering the characteristic X-ray spectra of the elements. A crystal reflects waves of given length  $\lambda$  only at the angles given by the equation  $n\lambda = 2a \sin \theta$ , where  $n$  is an integer,  $a$  the distance between successive planes in which the atoms of the crystal are arranged, and  $\theta$  is the "glancing" angle between the incident beam and the crystal face. If homogeneous radiation coming from a fine source falls on a crystal it is only reflected in the neighbourhood of a certain line on the crystal, this line being such that the incident beam there makes the proper angle with the crystal face. The reflected beam falls on a photographic plate and produces a fine line on it. Our present object is to discuss the structure of this line, which is of course not infinitely narrow. This can be done without calculation. First consider the effect of the outermost plane of the crystal on radiation coming from a point source. Each atom scatters a certain amount of radiation into a small spherical wave. These scattered wavelets reconstruct themselves into

\* Moseley & Darwin, *Phil. Mag.* vol. xxvi. p. 210 (1913).

† Moseley, *Phil. Mag.* vol. xxvi. p. 1024 (1913).

a single wave coming as though from  $I_1$  the image of the source  $O$  in the plane (see fig.). The second plane similarly gives a wave coming from  $I_2$  the image of  $O$  in the second plane. This wave is a little weaker than the first, because the radiation is absorbed in passing twice through the first plane. The same argument applies to all the lower planes. Thus the effect at any point  $P$  is simply that of a set of spherical waves starting in phase together from  $I_1 I_2 \dots$ . But this is the same as the effect when a plane wave falls perpendicularly on a plate in which small holes are made at  $I_1 I_2$ , etc. The intensity at any point  $P$  is simply the intensity of the lateral spectra of the point grating. Observe



that the glancing angle is now the angle measured in the usual way from the normal. Let us now suppose the radiation to be monochromatic, and find the diffraction pattern in the neighbourhood of the  $n$ th lateral spectrum. The simplest way of seeing its nature is as follows. The waves from  $I_1 I_2 \dots$  will produce the same effect if, instead of starting in phase together, each starts at phase  $2n\pi$  behind the last. Thus the incident wave on the left of  $I_1 I_2$  may be imagined to be turned round through an angle  $\theta$  where  $n\lambda = 2a \sin \theta$  ( $2a$  is the distance between adjacent holes). The phase difference between the waves going from two neighbouring holes in any direction near  $P$  is now small, so that the holes may be

replaced by the line joining them. Thus the pattern at P is simply the diffraction pattern from a fine line one end of which  $I_1$  is sharp, while the effect on the other side falls off exponentially. In conformity with our assumption the amplitude of the wave coming from a depth  $z$  below  $I_1$  is to be taken as  $e^{-\mu z \operatorname{cosec} \theta}$  of that coming from  $I_1$  ( $\mu$  is the absorption coefficient for intensity). The structure that will be observed is thus a band, on one side of which is the diffraction pattern of a straight edge, while in the other direction the intensity falls off exponentially. In any manageable experiment the scale of the diffraction pattern would be only a few seconds, and would be entirely masked by the finite size of the source. For very hard rays the exponential diminution in intensity should be observed. It may easily be seen that at a distance  $\sin \theta \cos \theta / \mu$  from the sharp edge, the intensity has fallen to  $1/e$ . Thus, for work with hard rays it would be essential to use a very dense crystal, or else to curtail the grating by using a thin one. The line on the photographic plate is, strictly speaking, a conic section and not a straight line.

It is convenient here to anticipate a future result (§ 6). We shall see that the X rays must be held to have a refractive index which differs from unity by about a millionth. On account of the refraction the position of the line on the photograph is slightly shifted. Let  $\lambda, \theta$  be the external wave-length and glancing angle,  $\lambda', \theta'$  the internal. Let  $1+p$  be the refractive index. Then  $\lambda = (1+p)\lambda'$  and  $\cos \theta = (1+p) \cos \theta'$  or  $\theta - \theta' = -p \cot \theta$ . The observed position of the line corresponds to  $n\lambda' = 2a \sin \theta'$ , while that which would be expected is given by  $n\lambda = 2a \sin \theta_0$ . So  $(1+p) \sin \theta' = \sin \theta_0$ , and so  $\theta_0 - \theta' = p \tan \theta$ . Thus the shift is

$$\theta - \theta_0 = -p \operatorname{cosec} \theta \sec \theta.$$

This result will be proved later *ab initio*.

#### 4. Quantitative Method.

We next consider the case where the reflexion is measured electrically. For this, the information required is quantitative. We shall first find the total energy reflected into the electroscope when monochromatic radiation falls on a crystal without any slits. As would be the case in most experiments, we shall suppose the electroscope to be so wide that all the reflected radiation is included; it is then unnecessary to allow for the fact that the distance of the electroscope is

finite, and complicated operations with Fresnel integrals are avoided.

It is not necessary to carry through all the details strictly according to the electromagnetic theory. These can be introduced later. Let us suppose that when a wave of length  $2\pi/k$  falls on an atom, the amplitude of the scattered radiation at unit distance bears to that of the incident a ratio  $f(\psi, k)$ , where  $\psi$  is the angle between the direction of observation and the incident beam.  $f$  is of the dimensions of a length. In accordance with §§ 11–13 it will be taken to be real, involving no change of phase. In addition to  $\psi$  and  $k$  it will depend on the direction of polarization of the incident beam. We shall suppose  $f$  so small that the wave scattered by one atom does not influence the amplitude of vibration of the radiating system in any other. As we shall see, there is an effect on the phase which can still be included. It will appear that there is definite experimental evidence that the scattering of one atom does affect that of others, because we shall find reason to believe that over a narrow range of angles of incidence the reflexion is nearly perfect; so we can only regard the present process as a first approximation. For simplicity we shall take a crystal composed of atoms of a single element, arranged in a single lattice, but this lattice may be cubic or parallelepipedal. We also neglect the temperature vibrations of the atoms. These omissions are very easily set right later.

### 5. Reflexion from a Single Plane.

We first find the reflexion from one plane of atoms. Let the incident beam be  $e^{ik(Ct-R)}/R$ , where  $R$  is the distance from  $O$  (see fig. p. 317). Taking  $C$  as origin,  $O$  is the point  $(0, 0, h)$ . To find the reflexion at angle  $\theta$  we take as point of observation  $\rho \cos \theta, 0, \rho \sin \theta - h$ , so that  $\rho$  is the distance from  $I_1$ . Then the point of geometrical reflexion  $A$  is  $(R \cos \theta, 0, 0)$  where  $h = R \sin \theta$ . Let there be an atom at  $R \cos \theta + \xi, \eta, 0$ . This atom will contribute a component

$$\frac{f(2\theta, k)}{R(\rho - R)} \exp ik(Ct - R_{\xi\eta} - r_{\xi\eta}),$$

where the quantities that do not vary rapidly have been replaced by their values at  $A$ , and  $R_{\xi\eta}, r_{\xi\eta}$  are the distances of  $\xi, \eta$  from  $O$  and  $P$  respectively. By expansion we find that

$$R_{\xi\eta} + r_{\xi\eta} = \rho + \frac{1}{2} \frac{\rho}{R(\rho - R)} (\xi^2 \sin^2 \theta + \eta^2),$$



so that the whole effect is

$$\frac{f(2\theta, k)}{\rho} e^{ik(Ct-\rho)} \frac{\rho}{R(\rho-R)} \sum \exp - \frac{ik}{2} \frac{\rho}{R(\rho-R)} (\xi^2 \sin^2 \theta + \eta^2).$$

Let  $M$  be the number of atoms per unit area. Then the number in an area  $d\xi d\eta$  is  $M d\xi d\eta$ . Since the phase variation between neighbouring atoms is small we can replace the sum by an integral, and get as the reflected wave

$$\begin{aligned} \frac{f(2\theta, k)}{\rho} e^{ik(Ct-\rho)} M \frac{\rho}{R(\rho-R)} \iint_{-\infty}^{\infty} \exp - \frac{ik}{2} \frac{\rho}{R(\rho-R)} (\xi^2 \sin^2 \theta + \eta^2) d\xi d\eta \\ = \frac{f(2\theta, k)}{\rho} e^{ik(Ct-\rho)} \frac{M \cdot 2\pi e^{-\frac{i\pi}{2}}}{k \sin \theta}. \end{aligned}$$

If  $N$  be the number of atoms per unit volume and  $a$  the distance between successive planes of the crystal,  $M = Na$ , and we have as reflexion coefficient,

$$f(2\theta, k) \frac{Na 2\pi e^{-\frac{i\pi}{2}}}{k \sin \theta} = -iq. \quad . \quad . \quad . \quad (1)$$

This expression is not perfectly general since  $q$  might be made greater than unity by increasing  $N$ . This would violate the conservation of energy. In actual matter this would be prevented, because the vibration of each atom would diminish those of its neighbours, so that we should have to regard  $f$  as dependent on  $N$ . Numerical calculation shows that  $q$  is of the order  $10^{-4}$ , so that the simple form

probably stands. The factor  $e^{-\frac{i\pi}{2}}$  is the converse of the quarter wave which has to be introduced into diffraction problems.

## 6. The Refractive Index.

If the factor  $f(2\theta, k)$  is replaced by  $f(0, k)$  the same radiation, represented by  $-iq_0$ , is scattered on the other side of the plane, so that the wave there is of the form

$$(1 - iq_0) \frac{e^{ik(Ct-R)}}{R} \quad \text{or} \quad \frac{e^{ik(Ct-R)} - iq_0}{R},$$

since  $q_0$  is small. This neglects the absorption in the plane

which cuts down the amplitude by a real factor  $b$ , so that the transmitted wave is

$$b \frac{\exp ik(Ct-R) - iq_0}{R}.$$

The effect in the second plane is due to the incident wave and to the wavelets scattered by the atoms of the first. We have above seen that these reconstruct themselves and produce a component in the primary wave. This reconstruction will not really be very perfect until four or five layers have been passed, but no great error is introduced by supposing that it happens at once. Taking into account the effect of the first plane on the emerging wave, we find that the second plane gives a reflexion

$$-iq b^2 \frac{\exp ik(Ct - \rho_2) - 2iq_0}{\rho_2},$$

where  $\rho_2$  is the distance from  $I_2$ . Proceeding in this way, we find that the  $s$ th plane gives an emerging wave

$$-iq b^{2s} \frac{\exp ik(Ct - \rho_s) - 2iq_0 s}{\rho_s}$$

and that beyond it the transmitted beam is

$$b^s \frac{\exp ik(Ct - R) - iq_0 s}{R}.$$

The intensity corresponding to this is  $\frac{b^{2s}}{R^2}$ . But the rays have traversed a thickness  $sa \operatorname{cosec} \theta$ , so we take

$$b^2 = e^{-\mu a \operatorname{cosec} \theta}.$$

The presence of the term  $iq_0 s$  implies a refractive index. For  $s = \frac{z}{a}$ , so that the wave is propagated in a new direction with a velocity different from that of light. The refractive index is

$$1 + \frac{q_0}{ka} \sin \theta \quad \text{or} \quad 1 + \frac{2\pi N f(0, k)}{k^2}. \quad \dots (2)$$

It should be observed that in the forward direction the wavelets scattered by the atoms are in phase together, whether the latter are arranged regularly or not. So this refractive index applies equally well to amorphous substances.

7. *Reflexion of Monochromatic Radiation.*

Returning to the reflexion we get as the whole reflected amplitude

$$-iq \frac{e^{ik(Ct-\rho_1)}}{\rho_1} \left( 1 + \exp \{ -\mu a \operatorname{cosec} \theta + ik(\rho_1 - \rho_2) - 2iq_0 \} \right. \\ \left. + \exp \{ -2\mu a \operatorname{cosec} \theta + ik(\rho_1 - \rho_3) - 4iq_0 \} + \dots \right),$$

where the slowly varying quantities have been replaced by their values for the first plane. As has been indicated, the whole radiation at a finite distance is the same as at an infinite, so that we may take the  $\rho$ 's as large as we please. Thus  $\rho_s = \rho_1 + 2as \sin \theta$  and the whole expression is

$$-iq \frac{e^{ik(Ct-\rho)}}{\rho} \left( 1 + \sum_1^\infty \exp -s \cdot \mu a \operatorname{cosec} \theta - sika2 \sin \theta - s2iq_0 \right) \\ = -iq \frac{e^{ik(Ct-\rho)}}{\rho} \left\{ 1 - \exp - (\mu a \operatorname{cosec} \theta + ika2 \sin \theta + 2iq_0) \right\}.$$

If  $ka \sin \theta$  is near  $n\pi$  this has a strong maximum. Let  $ka \sin \phi = n\pi$ . Then  $ka \sin \theta = n\pi + ka \cos \phi (\theta - \phi)$  and the amplitude is

$$-iq \frac{e^{ik(Ct-\rho)}}{\rho} \left\{ \mu a \operatorname{cosec} \phi + i[2ka \cos \phi (\theta - \phi) + 2q_0] \right\}.$$

Corresponding to this we have an intensity

$$\frac{q^2}{\rho^2} \left\{ (\mu a \operatorname{cosec} \phi)^2 + [2ka \cos \phi (\theta - \phi) + 2q_0]^2 \right\}. \quad (3)$$

This has its maximum at  $ka \cos \phi (\theta - \phi) + q_0 = 0$ . If  $q_0$  is replaced by its value in terms of the refractive index, the expression at the end of § 3 can be recovered.

Suppose now that we measure the ionization in an electro-scope of length  $l$  and sufficient breadth to include the whole beam. The effect then is

$$\frac{Il}{\rho} q^2 \int \frac{d\theta}{(\mu a \operatorname{cosec} \phi)^2 + 4[ka \cos \phi (\theta - \phi) + q_0]^2},$$

where  $I$  is the intensity of the incident beam

$$= I \frac{l}{\rho} q^2 \frac{\pi}{\mu a \operatorname{cosec} \phi \cdot 2ka \cos \phi},$$

which reduces to

$$I \frac{l}{\rho} \frac{f^2(2\theta, k)}{\mu} N^2 \cdot \frac{1}{2} \lambda^3 \operatorname{cosec} 2\phi. \quad (4)$$

### 8. Effect of a Slit.

This expression, like that for reflexion from one plane, is not general because  $N$  may be so large that the reflexion would be greater than the incident beam and the energy would not be conserved. In reality, this would be avoided by the atoms influencing one another's scattering. The comparison with experiment (§ 14) shows that this is in fact the case, and we must see how. We have so far worked with an unlimited primary beam. Obviously the same result holds if a slit is introduced so broad that it does not cut out any of the radiation near the reflexion angle. The question arises, how narrow may this slit be before the reflexion suffers? This question may be answered by reference to the figure (p. 317). In front of each of the apertures  $I_1, I_2, \dots$  in the direction of  $P$ , supposed at infinite distance, must be introduced a slit. Each slit only has reference to its own aperture and is opaque to the waves from the others. In a direction near  $P$  the intensity will be given by the intensity in (3) multiplied by the intensity in this direction corresponding to a single slit. Suppose that the slit is placed symmetrically with regard to the spectral line. For any reasonable values the breadth of the diffraction pattern is much greater than that of the maximum in (3). Thus the condition to be satisfied is that the slit is to be of such a width that the intensity has its full value in the central line. Taking roughly the first maximum in a

Cornu spiral we find  $s^2 \cdot \frac{k}{\pi r} = 6$ , where  $s$  is the slit's breadth and  $r$  its distance from the source. We can now deduce an upper limit to the reflexion. Taking  $r = 30$  cm. and  $k = 10^9$  for medium X rays, we find that all the reflexion occurs within an angular breadth of about  $5''$ . If the observed reflexion is more than the whole amount included within  $5''$ , it is a sign that the simple theory will not hold, and that in an improved theory which takes account of the influence between atoms, the reflexion must be spread out in a broader pattern than indicated above.

### 9. Heterogeneous Radiation.

The transition from monochromatic radiation to the general "white" radiation is simple. Let the amplitude be represented by

$$\int_0^\infty \left[ \phi(k) + i\psi(k) \right] \frac{e^{ik(Ct-R)}}{R} dk.$$



The intensity corresponding to this will be proportional to

$$\frac{1}{R^2} \int_0^\infty (\phi^2 + \psi^2) dk \quad \text{or} \quad \frac{1}{R^2} \int_0^\infty u_k dk.$$

The reflected amplitude is

$$\int_0^\infty [\phi(k) + i\psi(k)] (-iq) \frac{e^{ik(Ct-\rho)}}{\rho} \frac{dk}{1 - \exp - (\mu a \operatorname{cosec} \theta + i \cdot 2ka \sin \theta + 2iq_0)},$$

corresponding to which there is an intensity

$$\frac{1}{\rho^2} \int_0^\infty u_k q^2 \frac{dk}{|1 - \exp - (\mu a \operatorname{cosec} \theta + i \cdot 2ka \sin \theta + 2iq_0)|^2}.$$

We suppose that  $u_k$  only varies slowly. As  $k$  varies the integrand has strong maxima when  $ka \sin \theta + q_0 = n\pi$ . Denote this value of  $k$  by  $k_n$  and near  $k_n$  put  $k = k_n(1 + x)$ .

Then the expression is approximately

$$\frac{1}{\rho^2} \sum_n u_n (q^2)_n \int_{-\infty}^\infty \frac{k_n dx}{(\mu_n a \operatorname{cosec} \theta)^2 + (2n\pi x)^2},$$

where the  $n$  subscript denotes that the quantity has reference to  $k_n$ . Performing the integration and putting in the value of  $q$ , we have

$$\frac{1}{\rho^2} N^2 a^2 2\pi \sum_n \frac{f^2(2\theta, k_n)}{\mu_n^*} \frac{1}{n^2} u_n,$$

or in terms of the more usual  $E_\lambda$  where  $E_\lambda d\lambda = u_k dk$ ,

$$\frac{1}{\rho^2} N^2 a^2 \sum \frac{1}{n^2} f^2(2\theta, k_n) \left( \frac{E_\lambda \lambda^2}{\mu} \right)_n \dots \dots (5)$$

By virtue of the assumption that  $u_k$  only changes slowly, the correction depending on the refractive index has been neglected. The expression would require a little modification for approximately monochromatic radiation.

It was by the above processes that the result quoted on pp. 230-231 of Moseley and Darwin was reached. Unfortunately there was made in that paper an assumption which cannot be maintained, viz. that the scattering and absorption are proportional. It would seem better to suppose them independent. The abbreviated proof there attempted cannot be maintained. In the first place, the area assigned for a Fresnel zone is incorrect and also the argument should be carried out with amplitude and not with energy. Amended in this way it gives the right result.

10. *Temperature Effect and Compound Crystal.*

We will next introduce an effect so far disregarded, the temperature correction. This, due to the fact that the atoms are at no time all in their planes, affects the reflexion from a single plane, but makes no further change. Of the displacements of the atoms, those in the plane produce no change of phase, and we only have to consider displacements out of the plane. The treatment here is rather different in detail from that of Debye\*. Let us suppose that the potential energy for a displacement  $\zeta$  is  $\frac{1}{2}\sigma\zeta^2$ . By the principle of equipartition out of the  $M$  atoms per sq. cm. a number

$$M\sqrt{\frac{\sigma}{2\pi kT}}\exp -\frac{1}{2}\frac{\sigma\zeta^2}{kT}d\zeta\dagger$$

are displaced a distance between  $\zeta$  and  $\zeta+d\zeta$ . These atoms are wrong in phase to an extent expressed by  $e^{-ik2\zeta\sin\theta}$ . There are a great many atoms in any region over which the phases of the undisturbed atoms are sensibly constant. The temperature effect can be thus expressed as a factor in the value of  $g$ , and this factor is

$$\sqrt{\frac{\sigma}{2\pi kT}}\int_{-\infty}^{\infty}\exp -\frac{1}{2}\frac{\sigma\zeta^2}{kT}-ik2\zeta\sin\theta d\zeta$$

$$\text{or} \quad \exp -\frac{1}{2}\frac{kT}{\sigma}(2k\sin\theta)^2 \quad \text{or} \quad \exp -\frac{1}{2}\frac{kT}{\sigma a^2}(2n\pi)^2.$$

This is for the amplitude, and so for the intensity the temperature vibrations introduce a factor

$$\exp -\frac{kT}{\sigma a^2}(2n\pi)^2. \quad . \quad . \quad . \quad . \quad (6)$$

It is the same for a given order of reflexion, but diminishes rapidly with the higher orders.

We next deduce the reflexion for a crystal composed of several similar interpenetrating lattices. Let  $N_r$  be the number of atoms per c.c. of the  $r$ th lattice,  $f_r$  their scattering effect, and let the planes of this lattice be at distance  $\alpha_r a$  from those of the first, let  $\sigma_r$  give the restraining force on the atoms. Then the expression

$$N^2 f^2 e^{-\frac{kT}{\sigma a^2}(2n\pi)^2}$$

\* Debye, *Ber. d. Deut. Phys. Ges.* 1913, p. 671.

†  $k$  is used in two different senses, but the difference will be clear.

must be replaced by

$$\left| \sum_r N_r f_r e^{-i2n\pi\alpha_r} e^{-\frac{kT}{2\sigma_r a^2}(2n\pi)^2} \right|^2 \dots \quad (7)$$

This applies to both monochromatic and white radiation.

### 11. *The Scattering of a Single Atom.*

We must now discuss the form of the function  $f$ . When a light-wave in which the electric vector is along  $x$  falls on a system capable of vibration, a wave is scattered which is greatest in amplitude in the  $yz$  plane, vanishes in the line of  $x$ , and in any intermediate direction is proportional to the cosine of the angle between that direction and the  $yz$  plane. In this way we find that in  $f^2(2\theta, k)$  there will be a factor  $\frac{1 + \cos^2 2\theta}{2}$  due to the two polarized com-

ponents of the incident beam. This gets rid of the polarization, and we need only consider the form of  $f$  in a plane perpendicular to the electric vector.

The atom consists of a positive charge and of electrons, but the former is much too heavy to scatter radiation and may be neglected. Though there can be little doubt that it does not represent the reality of the case, we shall proceed according to the ordinary electromagnetic theory, as applied to dispersion. In optics this gives satisfactory results, and it should do so here as well. Let  $e, m$  be charge and mass of an electron, and let the forces which hold it in equilibrium have a "stiffness"  $mk_0^2 C^2$ , so that the emission wave-length is  $2\pi/k_0$ . Under the action of an electric force  $X$  the electron moves according to the equation

$$m\ddot{\xi} + mk_0^2 C^2 \xi - \frac{2}{3} \frac{e^2}{C^3} \ddot{\xi} = eX.$$

Then if  $X = e^{ik(Ct-x)}$  we have

$$\xi = \frac{eX}{m(k_0^2 - k^2)C^2 + \frac{2}{3}e^2 k^3 i}.$$

At a great distance  $r$  in the plane of  $yz$  this gives a wave of amplitude

$$\frac{e^2 X e^{-ikr}}{m(k_0^2 - k^2)C^2 + \frac{2}{3}e^2 k^3 i} \frac{k^2}{r} \dots \quad (8)$$

If we take this expression and add together the terms for each electron in the atom, and substitute in (2) for the

refractive index, we get the Selmeyer dispersion formula. Since it is quite possible that  $k$  should be greater than  $k_0$  for all the electrons, the refractive index may quite well be less than unity.

## 12. Mutual Action of the Electrons in an Atom.

For the electrons which contribute the light spectrum  $k_0$  is very much smaller than  $k$  and may be neglected. Sir J. J. Thomson\* assumes this for all the electrons. The imaginary term is very much smaller than the real, so he puts  $f = -\frac{e^2}{mC^2}$  for each electron, and uses this expression to estimate the number of electrons in the atom, from the known scattering of an amorphous substance.

But without further discussion this is not legitimate, even assuming that all the  $k_0$ 's are negligible. For some of the electrons are crowded very close together, probably within a distance of about  $5 \times 10^{-10}$  cm.†, which is fairly small compared with the wave-length of the radiation. Now it is well known that a small body scatters light of short wave-length much more completely than long. We must make certain that this will not be the case here. Suppose we have  $\nu$  electrons crowded together at points  $x_1 y_1 z_1$  &c., the scale of their distances being measured by a length  $\rho$ . Let the external radiation be  $X = e^{ikCt}$ . This sets all the electrons in vibration, and the motion of each influences the others. Let  $\xi_1$  be the displacement of the first electron. Then  $\xi_1$  is of the form  $\frac{A_1}{e} \exp ikCt$ . At a near point this electron exerts a force

$$\frac{3x - x_1^2 - r^2}{r^5} A_1 e^{ikCt}.$$

Similarly for the others. The whole electric force on the first electron then is

$$\left(1 + \sum_2^\nu \frac{3(x_s - x_1)^2 - r_{1s}^2}{r_{1s}^5} A_s\right) e^{ikCt} = \frac{m\ddot{\xi}_1}{e} = -\frac{mk^2C^2}{e^2} A_1 e^{ikCt}.$$

We are neglecting the restraining forces on the electrons,

\* J. J. Thomson, 'Conduction of Electricity in Gases,' p. 326.

† Calculated on Bohr's theory for a ring of 4 electrons in a sodium atom.



and also the reaction of their radiation on their motion. We thus get a set of equations

$$-A_1 = \frac{e^2}{mk^2C^2} \left( 1 + \sum_2^{\nu} \frac{\beta_{1s} A_s}{\rho^3} \right),$$

where  $\beta_{1s}$  is a quantity depending on the arrangement and is of the order of unity. The whole amplitude of the radiation scattered to a distant point in the  $yz$  plane is

$$\frac{k^2}{r} e^{ik(Ct-r)} \sum A_s.$$

The character of the solution of the simultaneous equations depends on the magnitude of  $\frac{e^2}{mk^2C^2} \frac{1}{\rho^3}$ . If it is small we get  $A_1 = -\frac{e^2}{mk^2C^2}$ , so that the scattered radiation is proportional to  $\frac{e^2}{mC^2}$ . On the other hand, if  $\frac{e^2}{mk^2C^2} \frac{1}{\rho^3}$  is large we can neglect the terms on the left, and we have a set of equations of the form  $1 + \sum_2^{\nu} \frac{\beta_{1s} A_s}{\rho^3} = 0$ . Whatever the solution may be, it will give  $A_s$  independent of  $k$  and proportional to  $\rho^3$ , so that the scattered radiation will be proportional to  $k^2 \rho^3$ . This is exactly the result found by Lord Rayleigh\* in his theory of the light of the sky.

Thus the question turns on the value of  $\frac{e^2}{mk^2C^2} \frac{1}{\rho^3}$ . Taking light of wave-length  $5 \times 10^{-5}$  cm. and  $\rho = 10^{-3}$  cm., we represent the effect of a molecule of the atmosphere. This gives  $\frac{e^2}{mk^2C^2} \frac{1}{\rho^3} = 18$ , which is probably large enough. For our inner ring of electrons we take  $\rho = 5 \times 10^{-10}$  and for soft X rays  $2\pi/k = 10^{-8}$ . Then  $\frac{e^2}{mk^2C^2} \frac{1}{\rho^3} = 6 \times 10^{-3}$ . This is small enough, so that we may assume that an atom scatters long waves to the same extent as short.

### 13. The "Excess" Scattering.

The waves scattered by the electrons in an atom combine to a certain extent so as to give a scattered radiation greater in intensity than is simply proportional to their number. For example, the electrons at distances  $5 \times 10^{-10}$  cm. apart would exert an effect almost proportional to the square of

\* Cf. Rayleigh, 'Sound,' vol. ii. p. 149.

their number. Consider the effect of an atom in a direction inclined to the incident beam at angle  $2\theta$ . Of the  $\nu$  electrons, all in any plane at angle  $\theta$  give waves in phase together. Let  $p_s$  be the distance of an electron from some plane drawn in this direction. The whole resultant amplitude is then proportional to  $\Sigma \exp -ik \cdot 2p_s \sin \theta$ . To find the corresponding intensity we multiply by the conjugate imaginary and get

$$\nu + 2 \Sigma \Sigma \cos 2k \sin \theta (p_s - p_t) \dots \dots (9)$$

This expression accounts for the phenomenon of the "excess radiation" which is observed in the scattering at small angles by an amorphous substance\*. For  $k$  is of the order  $10^9$  for medium rays and  $p_s - p_t$  is at most  $10^{-8}$ , so if  $\theta$  is less than  $5^\circ$  every single electron in the atom contributes to the excess. At broader angles a few of the outermost electrons fail to help, but there will be still a number of contributors. Finally, when  $\theta = \frac{\pi}{2}$  only those contribute which are less than a quarter wave apart. Moreover, the same excess will be exhibited at a broader angle for the softer rays†.

When we come to consider the reflexion of a crystal we get the formula

$$\nu + 2 \Sigma \Sigma \cos \frac{2n\pi}{a} (p_s - p_t).$$

We may probably assume that the interiors of the atoms are oriented in all directions, since any forces which were strong enough to turn them into one direction, would probably show some optical effect, and this would mean that a cubic crystal should show double refraction. So we may suppose that the average of  $p_s - p_t$  is independent of  $\theta$ . Then the excess radiation contributes a constant factor to the reflexion in each order, but that factor is greater for the lower than for the higher orders.

Using the value of  $f$  as above, we arrive at the following formula for the reflexion of white radiation from a crystal composed of one lattice.

\* Barkla, *Phil. Mag.* vol. xxi. p. 270 (1911); Crowther, *Proc. Roy. Soc. A.* vol. lxxxv. p. 29 (1911).

† Various hypotheses have been put forward to account for the excess radiation, by J. A. Crowther (*Proc. Camb. Phil. Soc.* xvi. p. 534, 1913) and by D. L. Webster (*Phil. Mag.* xxv. p. 234, 1913). The last assumes it due to the cooperation between electrons. He does not distinguish between electrons in the same and in different atoms. Except in the region of the diffraction pattern of the primary beam, the latter are as likely to contribute a negative as a positive term to (9).

$$\frac{N^2 a^2}{\rho^2} \frac{1 + \cos^2 2\theta}{2} \sum_n \frac{1}{n^2} \left( \frac{e^2}{mC^2} \right)^2 \left( \nu + 2 \sum \cos \frac{2n\pi}{a} (p_s - p_t) \right) e^{-\frac{kT}{\sigma a^2} (2n\pi)^2} \left( \frac{E \cdot \lambda^2}{\mu} \right)_n \quad (10)$$

#### 14. Comparison with Experiment.

We will now compare this result with experiment, and shall find that our formula gives more reflexion than is possible. The comparison is with the experiments on rocksalt in Moseley and Darwin\*. The Braggs' work† has shown that Na and Cl both contribute to the reflexion, and for a rough comparison it will be good enough to take them as identical and deduce the average character of the two. They are then arranged on a simple cubic lattice. Using Millikan's‡ most recent values, we find that the side of the lattice  $a$  is  $2.81 \times 10^{-8}$  cm. and  $N$  is  $4.50 \times 10^{22}$ . The work of Moseley§, combined with that of Barkla||, shows that over a considerable range of the softer rays  $\mu$  is exactly proportional to  $\lambda^{5.2}$ . For very much harder rays this is confirmed by a single experiment in Moseley and Darwin¶. We shall assume this relation to hold. Of the other quantities in (10)  $\sigma$  can be found from the infra-red absorption band of rocksalt. If  $M$  be the average mass of an atom  $M\ddot{\zeta} + \sigma\dot{\zeta} = 0$  expresses the vibration of an atom. The wavelength of the absorption band is  $54 \mu^{**}$ . From this  $\sigma$  can be found. The temperature factor is found to be 0.96 for the first order, 0.86 for the second. For the sixth it is 0.27. The smallness of the effect accounts for its not having been hitherto observed. The excess radiation factor is much in doubt until the structure of the atom is better known. The simplest process is to take the ratio of first to second order from the heights of the "peaks" in Bragg's experiments. Using this, it is a simple matter to disentangle the separate orders, and the work shows that a considerable error in estimating the strength of the second order will not change the result very much. No allowance can be made for the polarization of the rays coming from the tube, as it is not known which are the components polarized. Taking as standard wave-length  $\lambda_0$ , that reflected in rocksalt (1, 0, 0) plane

\* *Loc. cit.* p. 219.

† W. L. Bragg, *Proc. Roy. Soc. A.* vol. lxxxix. p. 248 (1913).

‡ R. Millikan, *Phys. Rev.* vol. ii. p. 109 (1913).

§ H. G. J. Moseley, *loc. cit.*

|| C. G. Barkla, *Phil. Mag.* vol. xxii. p. 396 (1911).

¶ *Loc. cit.* p. 220.

\*\* Rubens and v. Baeyer, *Berl. Ber.* 1913, p. 802.

at  $4^\circ$ , we have  $\lambda_0 = 3.92 \times 10^{-9}$  cm. We then get a curve of intensity given in the following table:—

$\lambda/\lambda_0$	$\frac{1}{2}$	$\frac{5}{8}$	$\frac{3}{4}$	$\frac{7}{8}$	1	$1\frac{1}{8}$	$1\frac{1}{4}$	$1\frac{1}{2}$	$1\frac{3}{4}$	2	$2\frac{1}{4}$
$E_\lambda$	3	10	32	68	100	104	99	79	48	22	11

By a rough quadrature it appears that about 7 per cent. of the radiation is contributed by the characteristic platinum radiations; and it happens that  $\int E_\lambda d\lambda$  is very nearly equal to  $E_0 \lambda_0$ , where  $E_0$  refers to the value at  $\lambda_0$ . In deducing this result it is assumed that the ionization is proportional to the energy. This assumption is rather doubtful, as we should expect that the secondary electrons from the softer rays would be so appreciably absorbed by the gas that they produce less than their due share of ionization.

Using this quadrature and the experimental value 0.0035 for the efficiency of reflexion at  $4^\circ$ , we can estimate the value

of  $\nu + 2 \Sigma \Sigma \cos \frac{2n\pi}{a} (p_s - p_t)$ . It is 26. But there is strong

reason to believe that the efficiency was overestimated. We have seen that, assuming the independence of scattering from separate atoms, the whole reflexion really only takes place within a breadth of about  $5''$ . If we assume that the radiation in this breadth is completely reflected, we arrive at

an efficiency  $\frac{E_0 \frac{d\lambda}{d\theta} \delta\theta}{\int E d\lambda}$ , where  $\delta\theta$  is  $5''$ . Using the quadra-

ture, this is  $\cot \theta \delta\theta$  or 0.0004. It is possible that when the reflexion becomes strong it is spread over a broader angle, so that we cannot conclude that the overestimate of efficiency is as great as suggested by this figure. It may be observed that the disagreement cannot be due to the less ionization by the softer rays, since the efficiency is measured by comparison with the *ionization* of the whole beam. It seems possible that in comparing two effects one of which is 300 times the other, there should be incomplete saturation in the larger.

Unfortunately the fact that the reflexion must be regarded as nearly perfect vitiates the formulæ for reflexion. It does not even appear why the second order should be so much weaker than the first. It is hoped to discuss this aspect of the matter in a future paper.



15. *The Absence of Resonance.*

A very interesting question arises with regard to the natural periods of the electrons. If there are such periods in the X-ray region it should be possible to observe a marked change in the refractive index in their neighbourhood. It should also be found that a substance scatters a particular wave-length much more efficiently than any other. The early work on refraction was all with heterogeneous rays and so cannot be taken as evidence, and no one has worked at the scattering of characteristic radiation. In Moseley's experiments the reflexion of the iron rays by potassium ferrocyanide was not specially strong, but we know it in all cases to be nearly as good as it can be. But in spite of the absence of direct evidence, it seems almost incredible that an increase of about a million times (which is what would be expected from (8)) should not affect the apparent absorption. Barkla found no special absorption by a substance of its own radiation, but that it needed for example rays as hard as those from nickel, to be strongly absorbed in iron. Superficially this bears some resemblance to a resonance effect. Indeed, before anything was known about the wave character of the characteristic rays, it might be thought of as an example of the fact that a strongly damped vibration responds best to a different frequency from that of emission. Even without further information this explanation would hardly work, for whatever the damping it will be found that the response is always nearly as good to the emission frequency as to the optimum. But Moseley's work has shown that the characteristic rays are extremely homogeneous, so that this view becomes quite untenable. On the whole it is simplest to suppose that Barkla's results depend in some way on an intermediate secondary electron. With regard to there being some real resonance effect, we can only hold that it seems rather improbable that it exists. If it does not, we must conclude that a substance radiating its characteristic X-ray spectrum is in some abnormal state. It would be exactly analogous to the fact that the hydrogen lines from a spectrum-tube are not absorbed in hydrogen.

*Summary.*

- (i.) The structure is discussed of the lines photographed by Moseley in his method of finding the X-ray spectra of the elements.
- (ii.) Proceeding on a theory exactly analogous to that of light, the intensity of reflexion is found both for monochromatic and for heterogeneous radiation.

- (iii.) The existence of a refractive index for both crystalline and amorphous substances is indicated by the theory.
- (iv.) The correction for the temperature vibrations is calculated.
- (v.) The effect of the several electrons in an atom is calculated, and is seen to account for the phenomenon of "excess radiation" observed in the scattering of X rays by amorphous substances.
- (vi.) The results are compared with the experimental results of Moseley and Darwin on rocksalt, and it appears that the reflexion is so good that the formulæ on which (ii.) is based must be inadequate in some particulars. The wave scattered by one atom disturbs the vibrations of the others.

My thanks are due to Prof. Rutherford for his kind interest in this research. Also to Mr. H. G. J. Moseley; several of the questions here considered arose from discussions with him.

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XXXV. *Anomalous Zeeman Effect in Satellites of Mercury Lines.* By H. NAGAOKA, *Professor of Physics*, and T. TAKAMINE, *Postgraduate in Physics, Imperial University, Tokyo* \*.

[Plate V.]

IN the present stage of our knowledge of the Zeeman effect, investigations as regards the separation of satellites of spectrum lines in a magnetic field are very scanty. Gehrecke and v. Baeyer † first measured the effect on the satellite of the green line of mercury in weak magnetic fields; similar measurements were made by Lunelund ‡ on several satellites of mercury lines, but as the strength of the field was limited to a few thousand gauss, the separation was generally proportional to the fields. Gmelin § was the first to notice an anomalous effect in the satellite +224 of the yellow line 5790, in which the separation was proportional to the square of the field; the observation was afterwards confirmed by Lunelund. This singular case was of special interest, as the principal line to which the said satellite belongs is,

\* Communicated by the Authors.

† Gehrecke and v. Baeyer, *Verh. d. Deutsch. Phys. Ges.* viii. p. 399 (1906).

‡ Lunelund, *Ann. d. Phys.* xxxiv. p. 505 (1911).

§ Gmelin, *Diss. Tübingen*, p. 41 (1909).

according to Zeeman and Gmelin, divided into a triplet showing remarkable dissymmetry. McLennan\* made a special study of the Zeeman effect of the green lines of mercury, and found that they were mostly divided into quartets in weak fields. Wendt† tried the effect of strong fields, and found that in place of the satellites there appear four new lines, which are nearly at a constant distance from the principal line. A complete study, following the course of satellites in a continuous manner from weak to strong fields, is still wanting; so that we are still in the dark as to the manner in which the satellites are gradually lost to view and the new lines make their appearance. Most of the experiments hitherto undertaken are confined to the separation of the principal lines; as to the behaviour of the satellites, it is briefly stated that they are so complicated in magnetic fields that the discrimination of the numerous lines as to their origin is extremely difficult. Tedious as it may at first appear, it would not be impossible to trace the course taken by the lines, if the separation in magnetic fields be simply proportional to the strength of the field, as in most of the spectrum lines hitherto investigated, however complicated the manner of separation may be. Our object in the present investigation is to follow the whole course of the change in the lines from weak to strong fields, and to show that the separation of the lines is not generally subject to the law of linear proportionality to magnetic force, including the singular case in which the change of wave-length is proportional to the square of the magnetic field, as one type of separation. We shall further show how the satellites gradually tend to osculate to the branches of the principal line, when the field is sufficiently increased.

The position of the satellites relative to the principal line was examined mostly by means of an echelon spectroscope constructed by Hilger, and described in our paper on crossed spectra. The spectrum produced by the echelon grating was not free from ghosts, so that it was sometimes necessary to obtain crossed spectra by means of another interferometer, when the existence of the line was doubtful. We tried the combination of echelon with a Lummer-Gehrcke plate, or with a sliding Fabry-Perot interferometer. Both apparatus can be used for the discrimination of false lines; but the air-plate was especially advantageous, as the thickness can be varied, and by this means doubtful lines more closely

\* McLennan, *Proc. Roy. Soc. A.* lxxxvii. p. 269 (1912).

† Wendt, *Ann. d. Phys.* xxxvii. p. 535 (1912).



examined by adjusting the positions of interference points with respect to the principal line. Moreover, it was easy to detect overlapped lines, which with a single apparatus would have been impossible. On this account, the Fabry-Perot interferometer was preferable to the Lummer-Gehrcke plate in the present experiment. The method was, however, inapplicable to weak lines, owing to loss of light in silver films, so that some may be missing in the crossed spectra.

The mercury lamp consisted of a vacuum capillary tube, whose ends were connected with wide tubes partly filled with mercury. The electrodes were sealed in them and came in contact with mercury. The tube was placed vertically between the poles of an electromagnet, and was excited by means of an induction-coil, whose primary was run by a single-phase current of 60 cycles per second, the mean strength varying from 3 to 6 amperes. In order to obtain a good image of the satellites, it was necessary to place in parallel a small air-condenser, which was connected with a coil of adjustable self-inductance. The electromagnet was specially designed to suit the purpose of investigating the Zeeman effect, having soft iron cores of 12 cm. diam. and coils of 3200 turns. For examining the transverse effect in uniform field up to 22 kilogauss, conical pole-pieces having vertical angle of about  $80^\circ$  were used, the air-gap being 6 mm. and the diameter of the end faces 20 mm. Special arrangement was provided for preventing the air-gap becoming wedge-shaped in strong fields, as is often observed in some electromagnets. For fields higher than 22 kilogauss, pole-pieces having vertical angle of  $112^\circ$  and end-faces of 4 mm. diam. were used, with air-gap of 4 mm.

The light from the mercury lamp in the air-gap was concentrated by two lenses on the slit of a collimator, and after prismatic resolution was projected on a slit placed in the focus of another collimator. It then traversed the echelon, and after passing through another lens was made parallel by a Zeiss microplanar of 5 cm. focal length, and then photographed by an anastigmatic objective by Goerz. A Wollaston prism was interposed between the microplanar and the photographic objective, so that the components parallel and perpendicular to the field could be photographed side by side, or one above the other, by proper adjustment. Following German authors, we shall hereafter denote these components by the letters  $p$  and  $s$ .

For photographing the green line, we used Agfa chromo-isolar plates and spectrum-panchromatic plates of Wratten and Wainwright; and for the violet line, process-plates.



The appearance of satellites was feebler in low than in high fields, so that the time of exposure varied with the strength of the field and the intensity of lines.

To clear up some doubts as regards the existence as well as the order of spectrum of lines, we interposed the Lummer-Gehrcke plate or the Fabry-Perot air-plate before the photographic objective, and obtained crossed spectra, which in nearly all cases decided the question, provided the lines were sufficiently strong. The interference points for the green line obtained by crossing the echelon with the Lummer-Gehrcke plate are shown in Pl. V. fig. 1, and those by combining the echelon with the Fabry-Perot plate in Pl. V. fig. 2.

In examining the Zeeman effect of the satellites, a series of photographs in successive stages of magnetic fields were taken with the echelon grating, in which the principal line appeared either in two consecutive orders of spectra or as a single line. One\* of us has already discussed the separation of the green line into a nonet, and its relation with the strength of the field, and found that the change in wavelength is proportional to it in all the different branches. By

applying Runge's rule, the value of  $\frac{e}{m}$  is  $1.780 \times 10^7$  E.M.U., which differs from that found by Cotton and Weiss for the same quantity ( $= 1.771 \times 10^7$ ) only by 0.5 per cent. Instead of measuring the field separately, it was deduced indirectly from the amount of separation of the principal lines.

The numerous photographs of the lines were examined micrometrically, and the position of the satellites in different fields plotted on a section paper, and the successive points joined by continuous lines. The process, though somewhat tedious, gave a rough delineation of the courses taken by different satellites, but it was not entirely free from ambiguity as to which branch of the separated satellite the points belong to, especially when different types of separation appeared, as in the satellites of the green line of mercury.

In addition to the photographs taken in uniform fields, it was thought desirable to have them also in heterogeneous fields, so that we can easily follow the course of the curve taken by lines of satellites in a continuous manner, the field strength being measured by the amount of separation in corresponding places, as already described. Evidently the points found from photographs in different uniform fields must agree with the course indicated by the photographs in heterogeneous fields; by following these two processes of

\* Nagaoka, *Phys. Zeit.* xi. p. 789 (1910).

finding the *position* by the one and the *course* by the other, we were finally led to the solution of the proposed problem.

The results are by no means so simple as in the Zeeman effect of most principal lines, in which they are divided into branches at regular intervals, however numerous their number may be. The anomalies in the Zeeman effect of satellites mainly consist in the complexity of the separated intervals, so that there is scarcely any simple proportionality with the field strength.

The reader will probably not be satisfied unless we give a complete set of photographs which were taken into account; but as a large number of plates will be necessary for this purpose, only some of the typical ones are given, for uniform as well as for heterogeneous fields; the latter will serve as a guide for judging the course taken by the different components. Sometimes there appeared faint traces of *s*-components in photographs of *p*-components, owing to imperfect polarization, and *vice versa*; but by taking proper precautions, these could be easily detected. Generally the definition of *s*-components was inferior to that of *p*-components, so that the complex separation of the satellites was difficult to decipher, and conclusive results for *s*-components must be reserved for further investigation.

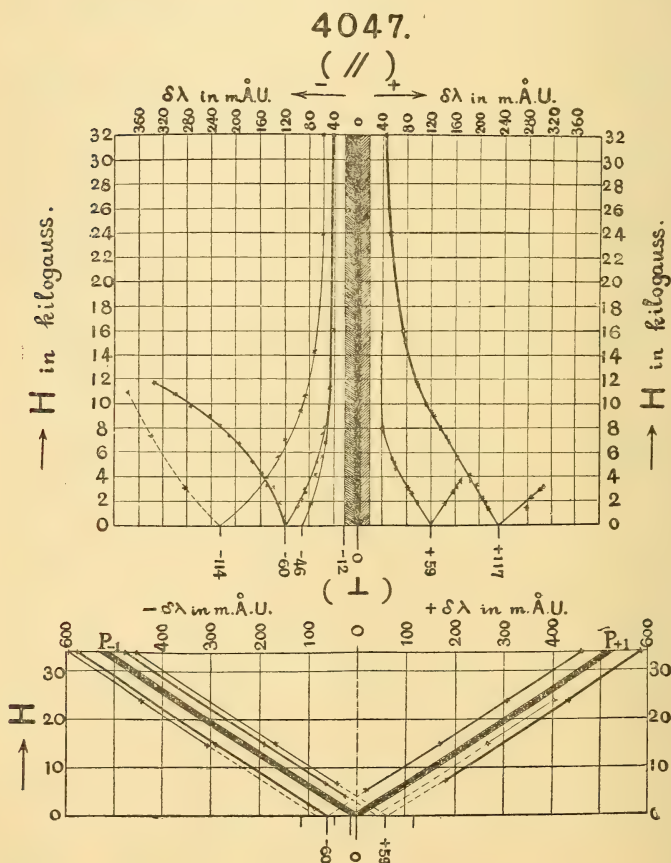
The present experiment is limited to the violet line 4047 and the green line 5461. The photographs in different fields are given in Pl. V, figs. 3-11, in which both *p*- and *s*-components are given. For mere qualitative inspection as to the course taken by the lines, the photographs in heterogeneous fields give a good illustration of the anomalies in the separation.

Arranging the photographs of the type given in these figures in proper order, we can graphically represent the change in the position of the satellites relative to the principal line by means of figs. 1 & 2, in which the abscissæ give the distances from the principal line, and the ordinates the strength of the field in kilogauss. The initial position of the satellites in  $H=0$  is taken from our measurements made on crossed spectra, obtained by means of the echelon grating and Lummer-Gehrcke plate. The length of the line drawn underneath is proportional to the intensity. The shaded portion shows the actual breadth of the line.

Referring to the *p*-components of 4047, we notice the dissymmetry in the intensity of the different branches. The satellites +59 and +117 are divided linearly proportional to the field so long as it is weak, but the + branch (*i. e.*, that in the direction of increasing wave-length) gradually

becomes weak as the field is increased, and can no more be observed above 4 kilogauss. The — branch, on the other hand, increases in intensity, especially for +117. The change in wave-length bears a linear relation to the field up to about 6 kilogauss for +59 and to 10 kilogauss for +117.

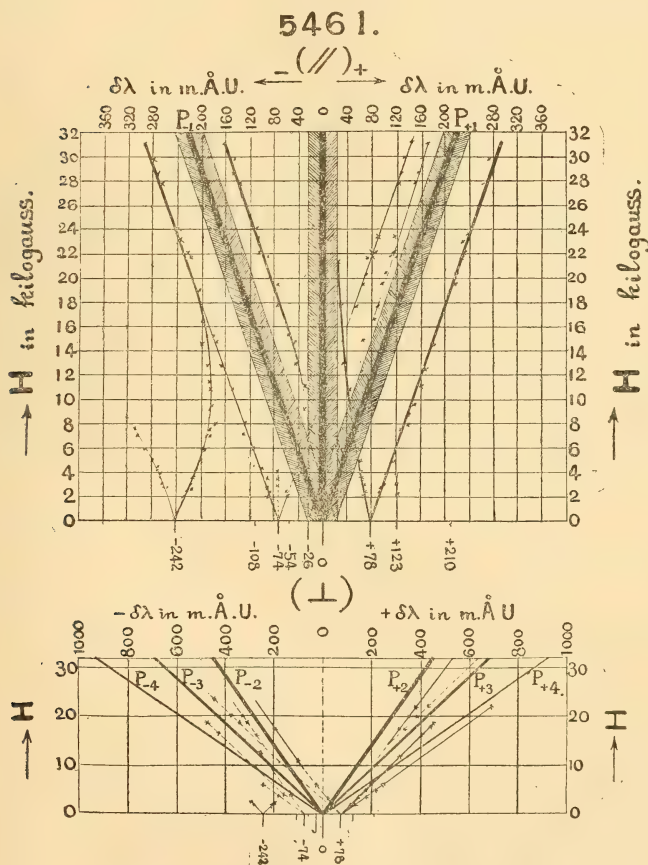
Fig. 1.



The change then becomes very slow, and the satellites approach the principal line asymptotically. The rapid decrease in the rate of change seems to be caused by the approach of the satellites to the principal line, and this seems to be the characteristic feature observed in this class of spectrum lines. On the side towards the smaller wave-length the change is even more marked than on the

other side. The linearity of the change in wave-length and the field is not obeyed in weak fields, so that the course taken by the branches of satellites is curved from the outset; in our experiments the lowest field was about 1500 gauss, where the separation is nearly normal; in strong fields they approach the principal line asymptotically.

Fig. 2.



We were not able to discriminate all the lines separately, so that doubtful curves are traced in dots. From the appearance of these curves, we can consider the branches of  $-46$ ,  $-60$ , and  $-114$  approximately as parabolas having vertical axis, and the  $-$  branch of  $-60$  as a parabola having horizontal axis. Thus for the  $+$  branch of the



satellite,  $\delta\lambda$  varies nearly as  $\sqrt{H}$ , while for the — branch  $\delta\lambda$  varies as  $H^2$ . The last branch is easily recognizable in Pl. V. fig. 4, taken in heterogeneous fields. The line becomes gradually faint in high fields, and vanishes just like the tail of a comet. Gmelin's observation in a satellite of the yellow line 5790 is therefore not at all singular; we shall perhaps meet with the same instance in different satellites. The ultimate position of the satellites in field of 30 kilogauss is as follows :—

— branch of	+ 117	:	+ 47	m. Å.U.
— " "	+ 59	:	+ 40 (?)	"
+ " "	{ - 46 (?) - 60	}	- 40	"
+ " "	- 114	:	- 57	"

The *s*-components cannot be distinctly photographed, so that the + and — branches of satellites thus far investigated are not markedly different as in the *p*-components. With 4047, the rate of separation becomes almost the same as that of the principal line from field of a few thousand gauss. We were not able to identify any except a single branch of —60 from the beginning, and it is difficult to say to which satellite the different branches given in the figure belong, on account of the intricate mixture of lines in weak fields. Judging from the asymptotic course given in fig. 1, it seems that

+ branch of	+ 59	lies	+ 68	from	$P_{+1}$
— " "	+ 59	"	+ 63	"	$P_{-1}$
+ " "	- 60	"	- 60	"	$P_{+1}'$
— " "	- 60	"	- 58	"	$P_{-1}'$

In addition to these, there are the lines

$$\begin{cases} + 38(?) & \text{,, } P_{+1} \\ + 44 & \text{,, } P_{-1} \\ - 76(?) & \text{,, } P_{-1}' \end{cases}$$

The existence of some of these lines is described by Wendt\*; the mean position of neighbouring lines observed by us coincides fairly well with his observation.

The numerous satellites of the green line of mercury are also characterized by the anomalous separation, but in high fields the tendency is the same as for the violet line. Some of the faint lines were difficult to observe, and the mode of separation must be postponed for future discussion.

\* Wendt, *loc. cit.*

The principal line is divided into a nonet, of which three belong to the  $p$ -components, and the remaining six to the  $s$ -components. The separation takes place regularly at equal intervals, and the lines are strong and broad, so that the branches of different satellites which cross each other are obscured in weak fields. Fig. 2 shows the separation for  $p$ - and  $s$ -components, the shaded portion representing the actual breadth of lines.

The satellite  $-242$  lying farthest from the principal line changes in a singular manner. It was already noticed by Lunelund that in fields of a few thousand gauss, the intensity of the  $+$  and  $-$  branches becomes equal, that of the former far exceeding that of the latter. In fact, the  $-$  branch becomes so faint that it is difficult to observe it beyond 10 kilogauss; the curve then begins to move in the opposite direction. This, however, goes on quite slowly, so that it is only in field of 24 kilogauss that the line returns to its initial position in zero field. The decrease in wavelength goes on steadily increasing at a constant rate, and with gradual increase in intensity. The type of separation in both branches is nearly parabolic, and resembles  $-60$  in 4047; the only difference being that the  $+$  branch, instead of osculating to the principal line, approaches the  $-$  branch of the satellite  $-74$ , which runs parallel to  $-$  component  $P_{-1}$  of the principal. The  $s$ -component of  $-242$  is a doublet of nearly equal intensity in weak fields, so that it is divided into a quartet as found by different investigators.

The linear relation between  $\delta\lambda$  and  $H$  is satisfied in the different branches of the satellite  $-74$ , which is apparently divided into a nonet. The separate lines all run parallel to the branches of the principal line, but are of unequal intensity. The one parallel to  $P_{-1}$  is very weak, and the  $+$  branch which runs parallel to  $P_{+1}$  is not very strong, and a portion, which probably passes through the principal lines, cannot be followed continuously on account of obliteration by the diffuse boundary of the principal line. The  $-p$  branch is strong in weak fields, but gradually diminishes in intensity, and ultimately becomes very faint as it approaches the  $+$  branch of  $-242$ , which on the contrary becomes very intense. It is questionable whether this branch of  $-74$  ceases to exist at this stage, or takes the same course as  $-242$  after merging into it. The increase in intensity can evidently be attributed to the resonance

between the branches of  $-74$  and  $-242$ , so that the energy imparted to different branches of  $-242$  is finally concentrated in the single branch. This point seems to have some signification in solving the problem of atomic structure. Quite close to the principal line lies a strong satellite in the position of  $-26$ . This satellite seems to be split into two branches, of which the negative branch rises almost in contact with the principal  $P_0$ , and after bending takes a course parallel to  $P_{-1}$ . On reaching this stage, the line becomes very intense, and in high fields it forms a companion with intensified  $-242$  on the negative side of the  $P_{-1}$  branch. This is a characteristic feature of the action of strong magnetic force on the green line. The other branch of  $-26$  seems to run almost parallel to  $P_{+1}$ , but is faint and difficult to observe.

The  $+$  branch of  $+78$  runs parallel to  $P_{+1}$  and becomes gradually strong, that it stands almost symmetrical with  $-242$  about the principal line  $P_0$ . The  $-$  branch of  $+78$  resembles the satellites of  $4047$ . It crosses  $P_{+1}$  and gradually approaches  $P_0$ , in which it is ultimately merged. The position of this line was at first difficult to decipher, but we noticed a slight dissymmetry in the separation of  $P_0P_{+1}$  and  $P_0P_{-1}$ , the latter being somewhat greater. This was afterwards found to be due to the presence of the  $-$  branch of  $+78$ , by which the centre of the line was slightly displaced towards the positive side, giving rise to an apparent dissymmetry about  $P_0$ .

Of the two  $s$ -branches of  $+78$ , one is difficult to trace, while another branch is somewhat curved. In high fields, the  $+$  branches are parallel to  $P_{+3}$  and  $P_{+4}$ , the  $-$  branches to  $P_{-2}$  and  $P_{-3}$ ; thus the separation is probably of the deformed sextet-type, of which the line  $4359$  of mercury is an example of regular type. Thus the effect of high field on the satellites of the green line is exactly similar in character with that of the violet line; the different branches of the satellites becoming ultimately parallel to those of the principal, the tendency to parallelism coming in the earlier stage for  $s$ -components than for the  $p$ -components.

The position of the branches parallel to those of the principal in  $p$ - and  $s$ -components is as follows :—

p-components .....	{		+ branch of + 78	:	+78 m. A.U. from P <sub>+1</sub>	}
	{		+ " " - 26 (?)	:	-40 (?) " " P <sub>+1</sub>	
	{		+ " " - 74	:	-70 " " P <sub>+1</sub>	
	{		- " " - 26	:	+54 " " P <sub>-1</sub>	
	{		+ " " -242	:	-78 " " P <sub>-1</sub>	
		{		- " " + 78	:	+24 (?) " " P <sub>0</sub>
s-components ...	{		inner + " " + 78	:	+56 " " P <sub>+3</sub>	}
	{		outer + " " "	:	+56 " " P <sub>+4</sub>	
	{		inner - " " "	:	+54 " " P <sub>-2</sub>	
	{		outer - " " "	:	+60 " " P <sub>-3</sub>	
	{		(?)	:	+80 " " P <sub>+2</sub>	
	{		+ branch of - 74 (?)	:	-40 (?) " " P <sub>+3</sub>	
		{		(?)	:	-44 (?) " " P <sub>-2</sub>

Preliminary examination of the strong satellites of the violet line 4359, which is a sextet, shows that the types of separation are not much different from those already found for the violet and the green line, and we hope to give a more exact description in the next communication.

The interesting experiments by Paschen and Back \* have an important bearing on the present investigation, but it is questionable if the theories proposed by Sommerfeld and by Voigt can be extended to the anomalous effect in the satellites of mercury lines. We have no doubt that the observed effects will be of some help in elucidating the nature of the satellites.

### Summary.

1. The separation of the satellites of the mercury lines 4047 and 5461 in magnetic fields is generally anomalous, and the change in wave-length is not linearly proportional to the strength of the field.

2. In high fields some branches of the satellites vanish, and the rate of change of wave-length with corresponding increase of the field becomes equal to that for the branches of the principal line.

3. The intensity of different branches of satellites is generally unequal.

4. For s-components, the state given in (2) is reached in fields weaker than for p-components.

August 7, 1913.

\* Paschen and Back, *Ann. d. Phys.* xxxix, p. 897 (1912).



XXXVI. *The Theory of Molecular Volumes.**By* GERVAISE LE BAS, *B.Sc.\**

## PART I.

THE EXISTENCE OF ADDITIVE RELATIONS IN  
MOLECULAR VOLUMES.

MUCH of the recent work in Physical Chemistry is connected with the correlation of the physical properties of matter and the chemical constitution of the molecules. The result is to show that the latter is reflected in the physical properties in a remarkable way, just as we may suppose that the nature of these is largely determined by the nature and build of the chemical molecules. It is usual to suppose that the physical properties of matter, chemically considered, are subject to at least three distinct influences :—

- (a) *An additive relation* which is due to the subdivision of the molecules into discrete portions called atoms.
- (b) *A number of constitutive influences* which are dependent upon the mode of arrangement of these atoms, and the particular distribution and force of residual chemical affinity.
- (c) Certain effects dependent upon the play of interatomic forces, or on the forces originating from the atomic or electronic units.

In *molecular volumes* we need concern ourselves only with the first two.

There has been a disposition during the last few years to regard with suspicion any attempt to correlate the molecular volumes of compounds and their chemical properties according to the method just outlined, owing to certain conceptions regarding the intimate structure of liquid having become current. This is certainly unnecessary, for it is now generally admitted that the co-volume, if it exist, is under conditions of vapour pressure, low as compared with the critical vapour pressure, proportional to the real molecular volumes. It follows that the molecular volumes of compounds at, say, the normal boiling-point, are also proportional to the real molecular volumes. The method of discussing these molecular volumes as originated by Köpp, and which is followed in the present paper, is thus quite justified.

\* Communicated by Prof. W. J. Pope, F.R.S.

We divide the influences operating on molecular volumes into:—

- (a) Additive,
- (b) Constitutive.

The first, as already stated, is an independent proof of the atomic division of matter. The latter is an important factor about which very little is known. An attempt is here made to elucidate some of these constitutive influences. We suppose that the acting forces are the repellent heat forces, following possibly some simple law. In the opposite direction are the conservative forces of chemical affinity. There will always be a balance between the two. Constitutive influences have the effect of modifying the latter according to the structural and other features of the molecules. The result is that a new equilibrium is obtained, and the molecular volume is correspondingly modified.

*A Periodic Relation between the Atomic Volumes.*

Kopp thought that the atomic volumes of the members of each family of elements have probably identical values (*Ann. Ch. Pharm.* xvi. p. 319).

This is not so. Thorpe has shown (*Trans. Chem. Soc.* 1880, xxxvii. p. 141, *ibid.* p. 327, and Kopp Memorial Lecture) that the volume of an element is a function of its atomic mass.

The necessity for changing many of the values has brought out this fact more clearly, that a periodic relation seems to exist between the atomic volumes according to the position of the corresponding element in the series. There are, however, remarkable divergences from the characters revealed by the well-known Lothar Meyer Table for Solids.

It will be seen that atomic volume variations occur at the boiling-point which are dependent on general characteristics of the molecules, but as a rule these do not influence the relations between their volumes. There are other cases where the atomic volume of an element undergoes a radical change according to its particular function. Thus hydroxylic oxygen has a volume  $2H(7.4)$  which is the same as the ester oxygen  $-OR$ , and the phenolic oxygen. Ethereal oxygen has a volume  $3H(11.0)$  and also carboxylic oxygen. When O is attached not to carbon but to S, P, or N, its volume changes to 8.3.

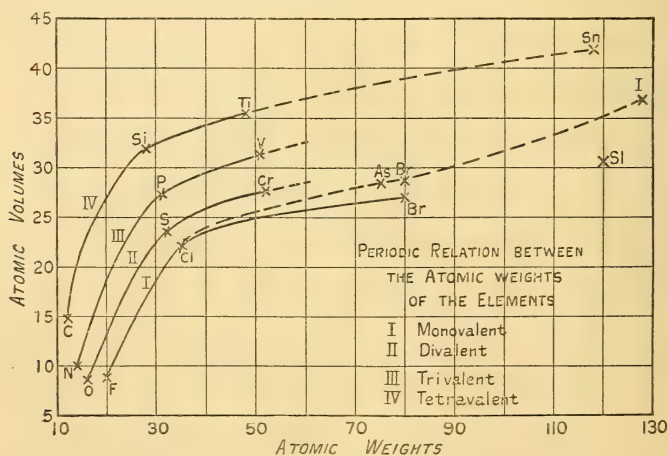
These facts lead us to suspect that the volume of an element may vary within certain limits, according not only to its position, but to its chemical function and relation to its surroundings.

This tendency to vary has been found chiefly among the O, N, S, and P atoms. Monovalent atoms do not apparently vary in this way.

*The Volumes of the Atoms in Compounds  
at the B.P.*

H 3.70									
	C 14.8	N 11.1		O <sub>G</sub> 7.4 (O')		F 8.7			
		15.6		11.0 > 0					
				: 0					
				O <sub>N</sub> 8.3					
	Si 32.0	P 27-28		S 22.1		Cl 22.1			
		27.1		25.6					
Zn 20.0	Ti 35.7	V 31.7	Cr 27.4						
		Ge 35.8	As 28.1	Se 28.0		Br 27-28			
		Sn 42.3	Sb 30.4	Te		I 37.0			
Hg 18.9									

If we arrange the volume of the atoms as shown in the combined state at the boiling-point on a diagram, we obtain the following remarkable series of curves.



If we examine the curves, we find that—starting from the members of the First Period, the numbers relating to the

atoms in each group arrange themselves according to their *fundamental valencies*, or increase continuously to the first group.

The *monovalent* atoms like F, Cl, Br arrange themselves on the lowest curve.

The *divalent* atoms like O, S, Cr arrange themselves on the next higher.

The *trivalent* atoms like N, P, V on the third; and the *tetravalent* atoms like C, Si, Ti on the fourth.

Moreover, the curves are similar.

*This shows that the volume is a function of the atomic weight on the one hand and the fundamental valency on the other, or at least increase continuously in each period.*

The points to notice are the increase with atomic weight in the different groups, and the decrease with the atomic weights in the different periods.

*Moreover, the volume is largely independent of the manner of linking and of changes of valency (vide prox.).*

The regularity is best shown in the atoms of the short periods and the even series of the long periods.

The Odd series of the long periods show some irregularity, although not of opposition to the above principle. Some allowance must be made for differences in environment. If we could obtain the volumes of a number of simple compounds of the elements like the chlorides, we might get a better idea of how the atomic volumes vary in this region.

Consider the elements in the Odd series of the second long period.

A more extended examination of the Halogen compounds than Thorpe has made and a systematic study of the organo-metallic derivatives would certainly lead to results of the highest interest.

#### *The Additive Factor in Molecular Volumes.*

That an additive factor in molecular volumes exists is undoubted, although an uncompromising Additive Theory such as was at first advocated by Kopp is untenable. The so-called constants which have from time to time been obtained can only be regarded as average numbers. They nevertheless possess a certain validity provided that we are careful to choose compounds within certain limits of complexity which are structurally similar.

The following simple substances (p. 348) illustrate the additive principle.

The same numbers are found to apply to organic and inorganic compounds indiscriminately.



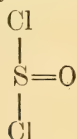
Mr. Gervaise Le Bas on the  
*Molecular Volumes of Simple Substances.*

Compound.	M.V.	ΣA.V.	Remarks.
$\text{N} \equiv \text{O} \equiv \text{N}^*$ .....	39.1	39.5	O 8.3
$\text{NO}_2, \text{NO}_2$ .....	64.0	64.4	
$\text{O}=\text{N}-\text{Cl}$ .....	46.0	46.0	
$\text{NH}_3$ .....	26.9	26.7	
$\text{NCl}_3$ .....	80.0	81.9	
$\text{N} \equiv \text{C}-\text{C} \equiv \text{N}$ .....	60.8	60.8	
$\text{H}-\text{O} \equiv \text{O}-\text{H}$ .....	23.4	24.0	
$<\text{C}=\text{O}$ .....	22.2	23.1	
$\text{O}=\text{C}=\text{O}$ .....	33.0	32.4	
$\text{O}=\text{S}=\text{O}$ .....	43.9	42.2	
$\text{CCl}_4$ .....	103.7	103.2	
$\text{COCl}_2 (\text{O}=\text{C} \cdot \text{Cl}_2)$ .....	70.1	70.0	O'' 11
$\text{CCl}_3\text{S} (\text{S}=\text{C} \cdot \text{Cl}_2)$ .....	81.7	81.1	
$\text{PCl}_3$ .....	93.4	93.3	
$\text{POCl}_3 (\text{O}=\text{P} \cdot \text{Cl}_3)$ .....	101.37	101.7	
$\text{PSCl}_3 (\text{S}=\text{P} \cdot \text{Cl}_3)$ .....	116.1	115.5	
$\text{POBrCl}_2$ .....	107.38	107.1	Br 27.5
$\text{CCl}_3\text{Br}$ .....	108.4	108.6	"
$\text{HgCl}_2$ .....	63.3	63.1	
$\text{HgBr}_2$ .....	75.9	75.9	
$\text{HgI}_2$ ..	92.8	92.9	
$\text{C}_3\text{H}_7\text{Cl}$ .....	91.7	92.1	
$\text{C}_3\text{H}_7\text{Br}$ .....	98.3	97.5	
$\text{C}_3\text{H}_7\text{I}$ .....	106.9	107.0	
$\text{CHCl}_3$ .....	84.5	84.8	
$\text{CHBr}_3$ .....	103.5	104.0	
$\text{C}_2\text{H}_5 \cdot \text{SH}$ .....	77.6	77.3	S=25.6
$(\text{C}_2\text{H}_5)_2\text{S}$ .....	121.6	121.6	

\* *Note.*—Evidence has since been adduced that both  $\text{N}_2\text{O}$  and  $\text{N}_2\text{O}_3$  are Ring compounds (see Journ. Chem. Soc.).

The following compounds which have been investigated by Thorpe deserve special treatment, because according to the old numbers they are possessed of constitutions quite out of harmony with chemical evidence generally and their genetic relations :—

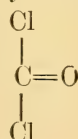
Thionyl Chloride.



S    25.6  
O''   8.3  
2 Cl 44.2

Calc. 78.1  
Obs. 78.0

Carbonyl Chloride.



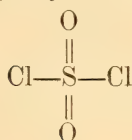
C    14.8  
O    11.0  
Cl<sub>2</sub> 44.2

Calc. 70.0  
Obs. 70.1

: O associated with carbon possesses the volume 11; in association with S, N, and P its volume is only 8·3.

Thus  $V \text{ N}_2\text{O}_4 \dots 2 \times 15\cdot6 + 4 \times 8\cdot3 = 64\cdot4$ . Obs. 64.

## Sulphuryl Chloride.



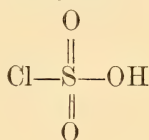
S	25·6
2 O''	16·6
2 Cl	44·2

---

Calc. 86·4

Obs. 86·3

## Chlorosulphonic Acid.



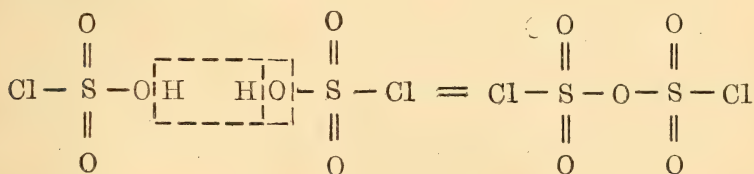
S	25·6	{	O' 7·4 H 3·7
OH	11·0		
2 O''	16·6		
Cl	22·1		

---

Calc. 75·3

Obs. 75·05

The transformation of the latter into disulphuryl chloride by the condensation of two molecules is a simple process:



This leads us to conclude that disulphuryl chloride contains two residues from chlorosulphonic acid or sulphuryl chloride joined on by an hydroxyl oxygen.

$$V \text{ SO}_2\text{Cl} = V \text{ SO}_2\text{Cl}_2 - V \text{ Cl} = 86\cdot3 - 22\cdot1 = 64\cdot2.$$

Allowing 5 units for hydroxyl oxygen :

2V	SO <sub>2</sub> Cl	128·4
	—O—	5·0

(SO <sub>2</sub> Cl) <sub>2</sub> O	133·4
Obs. ...	133·5

Compare the volume of  
CH<sub>3</sub>.CO—O—CO.CH<sub>3</sub>  
(*vide prox.*).

These conclusions are opposed to those obtained by Thorpe on the basis of Kopp's numbers, but are more in harmony with chemical evidence (see Thorpe, Proc. Roy. Soc. clx. 1875, and Trans. Chem. Soc. 1880).

The following transformations are also interesting :—

## Acetic Acid.



$$\text{V CH}_3 \quad 25\cdot9$$

$$\text{CO}'' \quad 25\cdot9$$

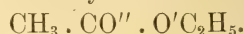
$$\text{O}'\text{H} \quad 11\cdot0$$

---


$$\text{Calc.} \quad 62\cdot8$$

$$\text{Obs.} \quad 63\cdot8$$

## Ethyl Acetate.



$$\text{V CH}_3 \quad 25\cdot9$$

$$\text{CO}_2 \quad 33\cdot0$$

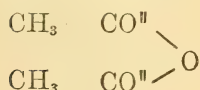
$$\text{C}_2\text{H}_5 \quad 48\cdot0$$

---


$$\text{Calc.} \quad 106\cdot9$$

$$\text{Obs.} \quad 106\cdot1$$

## Acetic Anhydride.



$$2 \text{ vols. CH}_3 \cdot \text{CO OH} \quad 125\cdot6$$

$$\text{less V H}_2 + \text{V O}' \quad 14\cdot8$$

---


$$\text{Calc.} \quad 110\cdot8$$

$$\text{Obs.} \quad 110\cdot0$$

## Acetyl Chloride.



$$\text{V CH}_3 \quad 25\cdot9$$

$$\text{CO}'' \quad 25\cdot9$$

$$\text{Cl} \quad 22\cdot1$$

---


$$\text{Calc.} \quad 73\cdot9$$

$$\text{Obs.} \quad 74\cdot05$$

## Ethyl Acetoacetate.



$$\begin{aligned} \text{Acetyl Group} \dots \text{V CH}_3 \cdot \text{CO}'' \cdot \text{Cl} - \text{V Cl} \\ = 74\cdot0 - 22\cdot1 = 51\cdot9. \end{aligned}$$

$$\begin{aligned} \text{V Ethyl Acetate} \dots \text{CH}_3 \cdot \text{CO} \cdot \text{OC}_2\text{H}_5 \text{ less V H} \\ = 106\cdot1 - 3\cdot7 = 102\cdot4. \end{aligned}$$

$$\text{V Acetyl Group} \dots \text{CH}_3 \cdot \text{CO} \dots \quad 51\cdot9$$

$$\text{V Group} \dots \text{CH}_2 \cdot \text{CO} \cdot \text{OC}_2\text{H}_5 \dots \quad 102\cdot4$$

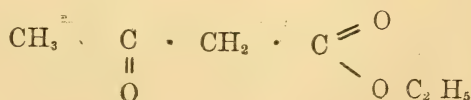
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$$\text{Calculated vol. of Acetoacetic Ester} \dots \quad 154\cdot3$$

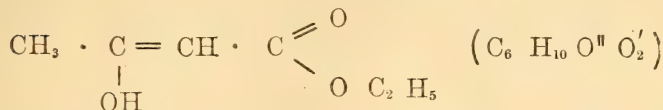
$$\text{Observed} \dots \quad 153\cdot7 \text{ (Schiff,}$$

$$\text{Ber. xix. p. 560.)}$$

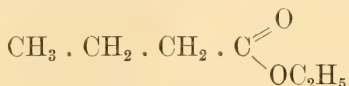
It is thus concluded that Acetoacetic ester contains the acetyl group ( $\text{CH}_3 \cdot \text{CO}'' -$ ), and its constitution is



If the compound possessed the "enolic" structure



it would show a similar volume to that of Ethyl Butyrate,



since  $\text{O}' = 2\text{H}$  and the double bond has no effect on the volume (*vide prox.*).

The volume of the latter is 150·5, which is different from the observed value by  $153\cdot7 - 150\cdot5 = 3\cdot2$ . Since acetyl (carboxylic oxygen)  $= 3\text{H}$ , the difference between  $\text{O}''$  (11·0) and  $\text{O}'$  (7·4)  $= 3\cdot6$ , a result which accounts for the difference in volume between Acetoacetic Ester and Ethyl Butyrate.

No one would be inclined to doubt the existence of an additive factor in molecular volumes from the evidence adduced. This has previously been recognized, but the agreement between calculation and experiment is closer than on the basis of the old numbers. Since Ring compounds, like the Aromatic, frequently possess side chains which are of similar constitution to those of Paraffin derivatives, it will be useful to give a few examples showing how such compounds are dealt with.

The old numbers  $\text{C} = 11\cdot0$ ,  $\text{H} = 5\cdot5$  were obtained by a comparison of Paraffin derivatives and Aromatic compounds, and thus are inaccurate. It will be found that the change in constitution marked by the arrangement of the 6 carbon atoms in a ring results in a very considerable compression of the molecule, without however affecting the relative volumes of C and H, which is a general principle.

*In Paraffin derivatives at the B.P.*

V C <sub>6</sub> H <sub>14</sub> .....	139·93	V C <sub>6</sub> H <sub>14</sub> .....	139·93
V C <sub>7</sub> H <sub>14</sub> .....	154·8	C <sub>6</sub> H <sub>24</sub> .....	132·40

Δ for C ...	14·87	Δ for H <sub>2</sub> ...	7·53
-------------	-------	--------------------------	------

Thus  $\text{C} = 4\text{H}$ ,

$$\text{or } \text{H}_2 = \text{V C}_6\text{H}_{14} - 6 \text{CH}_2 = 139\cdot90 - 132\cdot6 = 7\cdot3,$$

$$\text{and since } \text{CH}_2 = 22\cdot1, \quad \text{C} = 14\cdot8,$$

which are similar numbers.

The relation  $\text{C} = 4 \text{H}$  is thus a fact.



*Aromatic Compounds at the Critical Point,*

$$\begin{array}{rcl} \text{M.V. } \text{C}_6\text{H}_6 & \dots\dots\dots & 256\cdot3 \quad \div 30 = 8\cdot54 \\ \text{C}_6\text{H}_{12} & \dots\dots\dots & 306\cdot7 \quad \div 36 = 8\cdot52 \end{array}$$

$$3 \text{ H}_2 \dots\dots 50\cdot4$$

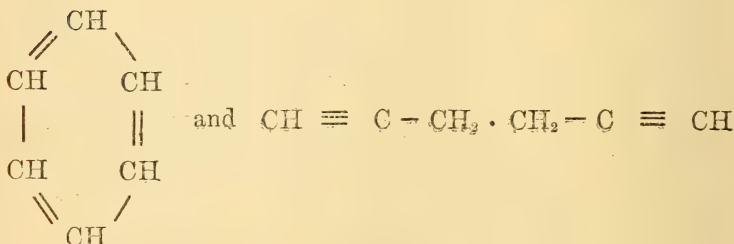
$$\text{H} = 8\cdot40. \quad (\text{Paraffin H } 9\cdot67.)$$

$$\text{C}_6 = \text{V C}_6\text{H}_6 - \text{V } 3\text{H}_2 = 256\cdot3 - 50\cdot4 = 205\cdot9.$$

$$\text{Thus } \text{C} = 34\cdot3 = 4 \times 8\cdot57. \quad (\text{Paraffin C } 38\cdot6.)$$

The formation of the ring has the effect of compressing the atoms while preserving their characteristic relative volumes.

The volume of benzene  $\text{C}_6\text{H}_6$  should thus differ from that of dipropargyl,  $\text{C}_6\text{H}_6$ , an open chain compound, by a large amount, since the constitutions of



differ considerably.

Volume of Hexane, $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3 \dots$	139.93	$\Delta$
„ Hexylene, $\text{CH}_2 : \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3 \dots$	132.4	7.53
„ Diallyl, $\text{CH}_2 : \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} : \text{CH}_2 \dots$	126.1	$2 \times 6.97$
„ Dipropargyl, $\text{CH} : \text{C} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C} : \text{CH} \dots$	110.3	$6 \times 7.4$
Volume of Benzene, $\text{C}_6\text{H}_6 \dots\dots\dots$	96.0	
Contraction.....	-14.3	

There is a very considerable contraction of  $-14.3$  at the normal B.P. for Ring structure in the Benzene nucleus. This is not due to unsaturation but to a very considerable compression of the atoms, due no doubt to mutual attractions of the carbons.

*The Additive Rule in Aromatic Compounds.*

Compound.	M.V.	ΣA.V.
Cinnamene, $C_6H_5 \cdot CH : CH_2$ .....	131.2	132.0
Phenyl Acetylene, $C_6H_5 \cdot C : CH$ .....	126.2	124.9
Anisol, $C_6H_5 \cdot OCH_3$ .....	125.5	125.6
<i>p</i> Cresyl M. Oxide, $C_6H_4(CH_3)OCH_3$ .....	148.0	148.0
Dimethyl Resorcin, $C_6H_4(OCH_3)_2$ .....	157.7	155.4
Benzaldehyde, $C_6H_5 \cdot CHO$ .....	118.4	118.7
Ethyl Benzoate, $C_6H_5 \cdot CO \cdot OC_2H_5$ .....	174.4	173.8
Phenyl Methyl Propionate, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CO_2Me$ ..	195.7	196.1
Cinnamic Methyl Ester, $C_6H_5 \cdot CH : CH \cdot CO_2CH_3$ .....	188.6	188.7
Phenyl Chloride, $C_6H_5Cl$ .....	114.6	114.9
Benzylidene Chloride, $C_6H_5 \cdot CH, Cl_2$ .....	154.7	155.2

The above numbers are in fairly good agreement. Many other cases occur, but since they are the subjects of constitutive effects they are left till later.

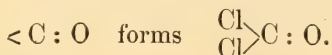
*The effect of Change of Valency and manner of Linking on Volume.*

A careful examination of the evidence will show that molecular volume is little, if at all, affected by the particular manner in which the linkages are distributed, or by changes in valency.

*Carbon C.*

Hitherto, carbon in combination has been thought to be exclusively quadrivalent. It is now known to be sometimes exceptionally divalent.

Thus in *Carbon Monoxide* it is Divalent, for



Also we may compare :—

*C Quadrivalent.*

Ethyl Cyanide,  $C_2H_5 - C \equiv N$ .

B.P. 97,  $d_4^{20}$  0.801,  $d_{B.P.}$  70098,  $V$  78.35

Ethyl Thiocyanate,  $C_2H_5 - S - C \equiv N$ .

B.P. 146,  $V$  100.1

*C Divalent.*

Ethyl Isocyanide,  $C_2H_5 - N = C$ .

B.P. 82,  $d_4^{20}$  0.801,  $V$  77.5

Ethyl Thiocarbamide,  $C_2H_5 - N = S = C$ .

B.P. 133,  $V$  99.3

There is certainly a small diminution in volume in the compounds belonging to the second column, and also a depression in the B.P. This corresponds with a displacement of N as well as a different function of C from that in the

*Phil. Mag.* S. 6. Vol. 27. No. 158. Feb. 1914. 2 A

first pair. This is also the case in the second pair, but sulphur also changes—in the opposite direction. The evidence is not conclusive. In any case the difference is small.

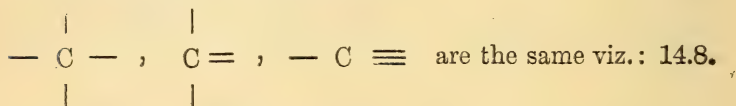
Closely associated with this subject is the question of *Unsaturation*.

The double bond (=) and triple bond ( $\equiv$ ) so-called, have very little effect on volume at the B.P., as is shown by the similar values obtained for C and H by a comparison of the Paraffins with the Olefins and Acetylenes and the values derived from a consideration of the *n* Paraffins alone. Thus the groups :



possess volumes in accordance with their composition.

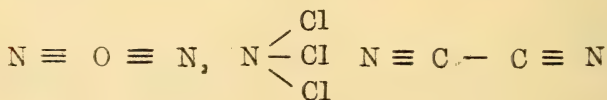
It follows that the volumes of



C has never any other value.

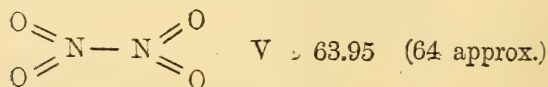
*Nitrogen N.* Free value 15.8.

*Trivalent* nitrogen possesses the volume 15.6 as is shown by the compounds



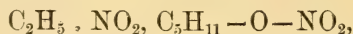
$\text{V}-\text{CN}$  is 30.4. Since C is 14.8,  $\equiv\text{N}$  is 15.6.

*Pentavalent N* has still the same value.



$\text{O}=8.3$ , and N is thus  $(64.0-33.2) \times \frac{1}{2} = 15.4$ .

The group  $\text{NO}_2$  is also found in



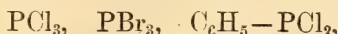
and its volumes in these compounds differ little from its volume in the free state.

In the Amines (Primary):— $\text{N}'''$  8.

„ (Secondary & Tertiary):— $\text{N}'''$  10–11.5.

*Phosphorus P.*

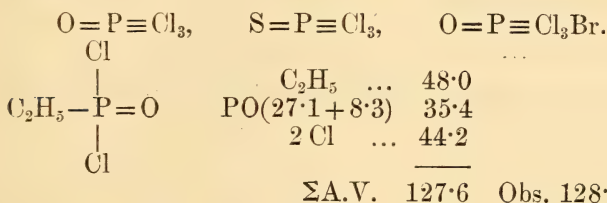
Trivalent P is certainly found in



and its volume therein is 27.1.

$$V \text{ PCl}_3 \ 93.34, \quad P = 93.34 - 3 \times 22.1 = 27.04.$$

Pentavalent P occurs in



P has the same value as pentavalent P.

The two extra valencies appear to have a different value in

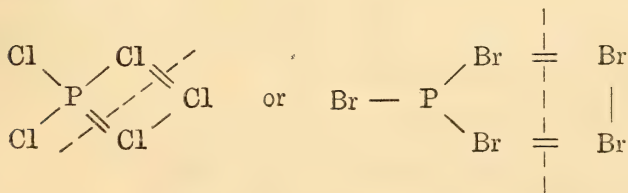
$\text{PCl}_5$ ,  $V \ 128.9$  (Prideaux).

$$\begin{array}{rcl} \text{PCl}_3 \ 93.4 \text{ (Thorpe)}, & 2 \text{ Cl } 44.2, & \Sigma \text{A.V.} \ 137.6 \quad \Delta \\ & \text{Observed} \ 128.9 & -8.7 \end{array}$$

So also in  $\text{PBr}_5$ ,  $V \ 157.3$  (Prideaux).

$$\begin{array}{rcl} \text{PBr}_3 \ 108.3 \text{ (Thorpe)}, & 2 \text{ Br } 57.0, & \Sigma \text{A.V.} \ 165.3 \\ & \text{Observed} \ 157.3 & -8.0 \end{array}$$

The difference is nearly the same in the two cases, and might be explained by assuming the possession of ring structure:—



This would also explain the instability of these compounds or liability to dissociation.



for the double bond is essentially weak.

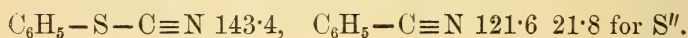
Again, in molecules  $\text{P}_4\text{O}_6$   $\text{P}_2\text{O}_4$  ring structure is present.

2 A 2



*Sulphur S.*

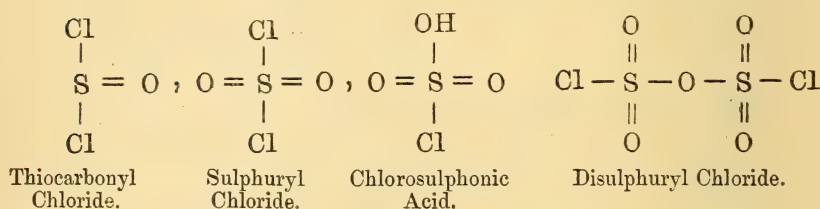
*Divalent* sulphur may have the volumes 22·1 and 25·6.



On the other hand



So also we obtain the value  $S=25\cdot6$  for  $S^{IV}$  and  $S^{VI}$ .



Thus *Tetravalent* and *Hexavalent* Sulphur are both 25·6.

In Carbon Disulphide,  $S=C=S$ , it seems to have the two values

$$V \ 62\cdot11, \ C + S' + S'' = 14\cdot8 + 22\cdot1 + 25\cdot6 = 62\cdot5.$$

As an alternative to this supposition, which was Kopp's, it is possible that if  $S_2$  has  $V \ 47\cdot7$ ,  $S$  has  $V \ 23\cdot8$ ; so that the two  $S$  atoms are equal.

On the other hand, the volumes of the atoms change for other reasons than those mentioned, reasons which are connected with constitution, considered in a wider sense than manner of Atomic linking.

Thus  $O$  may have the values 7, 11·0, and 8·3.

$S$  may have the volumes 22·1 and 25·6.

$N$  may have the volumes 8·6 and 11·0 (in amines) and also 15·6 in other compounds.

XXXVII. *The Anhyseretic Magnetic Properties of Iron and Nickel.* PART I. *The Relation of Magnetic Intensity to Field Strength and Temperature.* By J. REGINALD ASHWORTH, D.Sc.\*

*Index to Paragraphs.*

- (1) Introduction and meaning of anhyseresis.
- (2) Methods of suppressing hysteresis.
- (3) Experimental considerations.
- (4) Choice of suitable alternating current.
- (5) Law of inverse relationship between strength of alternating current and intensity of magnetization.
- (6) Construction of anhyseretic isothermals for iron and nickel.
- (7) Construction of anhyseretic isodynamics for iron and nickel.
- (8) Suppression of the critical temperature in nickel.
- (9) Application of Frölich's equation to anhyseretic isothermals and the proportionality of his constant to the absolute temperature.
- (10) Discussion of the equation and the relationship of Curie's Constant to the ferro-magnetic Constant.
- (11) Analogy to van der Waal's equation to the fluid state.
- (12) Comparison of the effects of alternating Currents and Temperature as evidence for a kinetic theory of magnetism.

(1) **T**HE phenomenon of hysteresis so greatly obscures the magnetic properties of a ferro-magnetic substance that it would appear desirable to eliminate it, or at least reduce it to a negligible quantity in making a study of these properties. In this paper I have confined myself to an investigation of the relation of magnetic intensity ( $I$ ) to field ( $H$ ) and temperature ( $T$ ) when hysteresis is suppressed. This state has been called by M. Charles Maurain "anhyseretic," and I have adopted this term for the condition in which hysteresis is under restraint without implying that it is altogether absent.

(2) For the purpose of reducing hysteresis several methods may be employed: the material may be subjected to vibrations and in the case of very soft iron this is effective; or alternating, or interrupted, currents may be used, the current being made either to traverse the substance under test, or to circulate round it, by running it through a solenoid; or again the temperature may be raised and lowered. In what follows, an alternating current was always employed for the suppression of hysteresis, its advantage being that it can be applied in a definite quantitative manner, and it does not affect the physical structure of the material.

The current, which was kept in action for the whole course of an experiment, was made to traverse the length of the

\* Communicated by the Author.

substance, thus setting up alternating circular fields in the metal, except in one group of experiments in which it was led into the surrounding solenoid, the alternating field thus acting to and fro in the direction of the magnetizing field.

(3) All the experiments have been carried out by the magnetometric method. It has the advantage over the ballistic method that it allows the observer to watch any change of magnetization continuously instead of intermittently. The magnetometer was an astatic one with a pair of vertical needles 0.7 centimetre apart and 13 centimetres in length suspended by a long silk fibre within a stout copper tube. The deflexions of the astatic pair were read by the usual arrangement of a reflected beam of light, the scale being about 1.7 metres from the mirror.

In the experiments on iron the solenoid was placed horizontally east and west and in such a position that its axis was on a level with the upper pair of poles of the needles, but in the experiments on nickel the vertical position was chosen in order to obtain a suitably large deflexion, and to minimise disturbances in the compensation due to certain thermal effects. In this position the vertical component of the Earth's force had to be balanced or allowed for. The solenoid itself was about 30 centimetres long, wound with a single layer of stout copper wire covered with asbestos, and was enclosed in a tubular sheath of copper, the whole being supported on two brass uprights.

When the apparatus had to be heated a row of broad flat Bunsen flames was applied underneath, the iron or nickel wire being suitably supported in the solenoid; on the other hand, when the wire had to be kept cold during the passage of a strong alternating current it was placed in the solenoid inside a glass tube through which a stream of cold water was allowed to flow. Each wire was 20 centimetres in length and was attached at one end to a stout piece of brass wire insulated with an asbestos sleeve; this brass wire served the double purpose of supporting the iron or nickel wire and of affording a return path for the alternating current. The iron wire was 0.057 centimetre in diameter and the nickel wire 0.050 centimetre, so that the dimension ratio was not less than 350.

When everything was in adjustment a continuous current was supplied to the solenoid the strength of which could be varied by means of a potentiometer, and the alternating current employed to annul hysteresis was derived from a generator having a frequency of 33 alternations per second.

The temperature was determined by a thermo-junction of platinum and platinum-iridium, one millimetre on the galvanometer scale corresponding to about 2° centigrade of temperature.

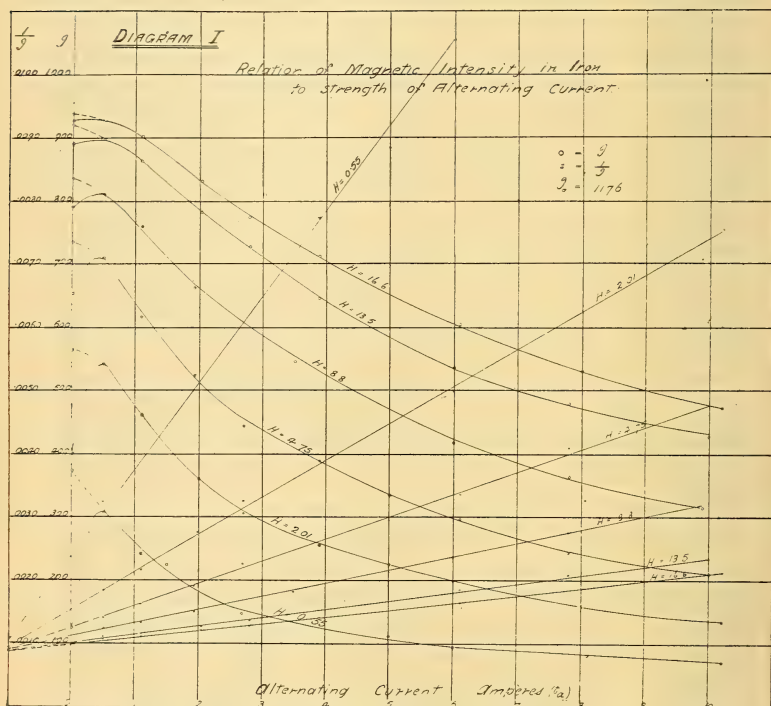
(4) The first step in the experimental work was the choice of a suitable strength of alternating current. Curves of  $I$  and  $H$  were constructed for alternating currents of gradually increasing strength and one virtual ampere was found to be sufficient to reduce the hysteresis, in iron, to a negligible quantity without appreciably lowering the intensity of magnetization at ordinary temperatures. This strength of current gave a maximum alternating field at the circumference of the iron wire of about 9 C.G.S. units, the field, of course, becoming less towards the centre. The effect of variation of frequency was tried and was found to be so small for an increase or decrease of 50 per cent. that any small change in the speed of the alternator was quite unimportant. Throughout the experiments a frequency of 33 alternations per second was maintained nearly constantly.

The suppression of hysteresis is more difficult in nickel than in iron, and a current of 2 virtual amperes only partially brought the magnetism to the anhysteretic state, and even currents twice as strong as this did not suppress hysteresis altogether.

(5) In connexion with this part of the investigation a series of experiments was made to trace the effect of increase in the strength of the alternating current on the intensity of magnetization of iron. The results are exhibited in the first diagram,  $I$  being plotted vertically against the strength of the alternating current  $i_a$  which was carried as far as 10 virtual amperes. Under the action of strong currents the wire had to be vigorously cooled with a current of cold water in the way referred to above. Constant fields of 0.55 to 16.6 C.G.S. units were applied in steps, while the alternating current was varied in strength at each step. The curves are of the hyperbolic type, and apparently an infinite current would be required to reduce the magnetic intensity to zero. At the beginning when no alternating current is running hysteresis is in unimpaired action and the intensity is low for a given very small force, but as the alternating current grows the freedom conferred upon the molecular magnets allows them to obey the applied field, and the intensity increases and reaches a maximum when  $i_a$  is about 0.5 ampere; for greater values of  $i_a$  the magnetic intensity smoothly declines at a diminishing rate. If the alternating current is now steadily



diminished the magnetic intensity retraces its path up to  $i_a = 0.5$ , but for lower values of  $i_a$  it continues to increase, and does not come back to the original low value. This is specially observable for low field strengths. There is, therefore, a *critical* strength of alternating current.



That the smooth parts of these curves are very nearly rectangular hyperbolas is shown from the fact that the reciprocals of  $I$  when plotted against  $i_a$  fall very nearly on straight lines, the only serious irregularity being for the curve of  $H=0.55$ , in which the observations would be affected by a larger error than for higher fields. These straight lines when prolonged backwards all meet approximately at a common point which is situated about 0.00085 on the scale of  $\frac{1}{I}$ , and at nearly -1.1 on the scale of  $i_a$ . It is possible to express these curves above the critical

current by an equation which for the larger values of  $H$  would have the form

$$H\left(\frac{1}{I} - \frac{1}{I_0}\right) = C(i_a + b),$$

where  $I_0 = 1177$ ,  $C$  has a mean value of  $1.8 \times 10^{-3}$ , and  $b = 1.1$ .  $I_0$  is the limiting intensity of magnetization for this sample of iron in the field employed.

Similar curves have been constructed for nickel, and the inverse relationship of  $I$  to  $i_a$  is again clearly in evidence, but the critical value of  $i_a$  is higher than for iron.

(6) Experiments were now instituted to trace the influence of variation of temperature on curves of  $I$  and  $H$ . The iron wire having been fixed in the solenoid a hysteretic curve was traced at the temperature of  $16^\circ$  centigrade, and immediately a curve of  $I$  and  $H$  was traced for the anhysteretic state. Pairs of such curves were successively traced for temperatures of  $16^\circ$  C.,  $645^\circ$  C.,  $721^\circ$  C., and  $776^\circ$  C.; at higher temperatures the intensity became very low, and the readings were not trustworthy. The numerical results are given in Table I.

The anhysteretic curves which are drawn in Diagram II., when compared with the hysteretic curves in Diagram III., show that the overlapping of the latter no longer exists. It is an effect of hysteresis. The anhysteretic curves, on the other hand, run independently of one another, the intensity of magnetization always becoming less for increasing temperatures.

When hysteresis is in action the magnetic intensity does not return to its old values on reducing the magnetizing force, but in the anhysteretic condition  $I$  is very nearly a single-valued function of  $H$ . Thus the complexities of the hysteretic isothermals disappear in the anhysteretic isothermals, and the latter are capable of being expressed by a simple formula which will be discussed at the end of the paper.

The same remarks apply equally to the isothermals of nickel. The numerical results are given in Table II. The anhysteretic isothermals alone are given in Diagram V., and for all of them the strength of the alternating current was 2.3 amperes.

TABLE I.

Hysteretic and Anhysteretic Intensity and Field at different Temperatures in Iron (C. G. S. units).

Hysteretic.

Anhysteretic.

Temp.	H.	I.	Temp.	H.	I.	I (calc.).
16° C.	0	40	16° C.	0	60	
	0.9	213		0.9	442	397
	2.9	652		2.9	628	656
	9.3	845		9.3	809	824
	13.2	879		13.2	852	853
	16.4	890		16.4	873	868
	17.5	904		18.3	879	874
	0	680		0	51	
645° C.	0	17	645° C.	0	11	
	0.9	261		0.7	179	143
	2.0	446		1.8	302	310
	2.9	532		2.7	380	393
	4.0	605		3.8	457	476
	5.8	667		4.7	502	525
	7.7	711		5.4	540	556
	9.5	735		6.2	569	584
	11.0	764		11.0	700	703
	14.5	788		14.5	746	737
	16.8	791		18.3	770	768
	0	336		0	12	
721° C.	0	21	721° C.	0	12	
	0.9	367		0.9	170	163
	2.0	481		1.8	264	263
	2.9	533		2.9	336	345
	4.0	564		4.0	401	400
	5.1	591		5.1	437	441
	5.8	606		5.8	465	461
	6.5	616		6.5	487	479
	7.7	627		7.7	504	503
	11.3	645		11.0	553	550
	14.5	662		17.1	599	595
	0	280		0	10	
776° C.	0	0	776° C.	0	19	
	0.9	320		0.9	122	117
	1.8	399		1.8	191	189
	2.9	433		2.9	233	248
	4.0	472		4.0	283	289
	5.1	487		5.8	330	334
	5.8	500		6.5	341	347
	6.5	504		7.7	361	362
	7.7	513		11.0	406	398
	11.3	537		14.5	412	422
	14.5	543		18.3	421	437
	0	214		0	17	

TABLE II.

Anhyseretic Intensity and Field at different Temperatures  
in Nickel (C.G.S. units).

Temp.	H.	I.	I (calc.).	Temp.	H.	I.	I (calc.).
21° C.	0.27	39	26	225° C.	0.27	32	20
	1.0	87	80		1.8	94	95
	2.2	135	139		4.1	138	158
	3.3	163	175		5.6	166	182
	5.2	199	215		8.6	206	213
	7.1	223	241		12.8	243	239
	9.4	250	262		14.3	255	245
	13.6	291	286				
	15.5	306	293				
139° C.	0.27	45	23	319° C.	0.5	27	27
	1.4	100	92		1.8	49	70
	2.6	128	139		3.3	76	97
	4.5	165	184		5.2	94	116
	5.2	...	196		7.7	118	130
	7.1	203	220		13.2	152	146
	9.4	228	239		14.7	161	149
	13.2	267	260				
	15.2	281	268				

Curves of anhyseretic susceptibility as a function of the magnetic intensity are drawn on Diagrams II. and V., and over the central range of intensities they approximate to rectangular hyperbolas\*.

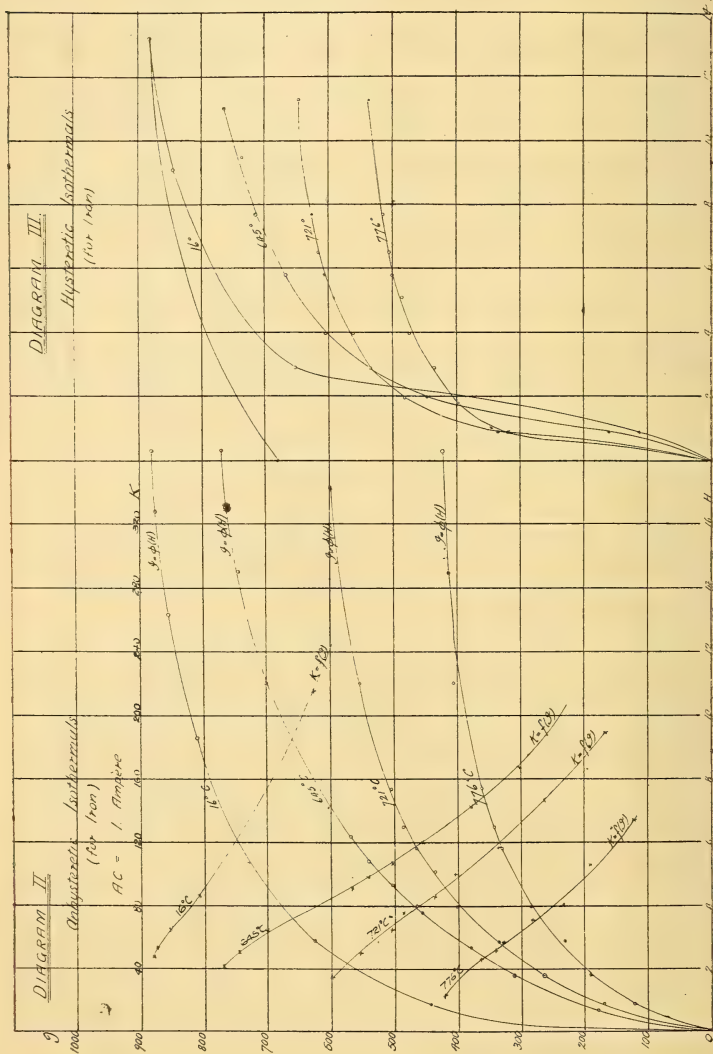
(7) With a sufficient number of anhyseretic isothermal curves it would be possible to construct isodynamic curves, or curves of  $I$  and  $T$  for constant fields, but separate experiments were instituted for the purpose. Simultaneous observations of  $I$  and  $T$  in a constant field were made as the temperature was raised to the highest point, and then lowered to the original point. The curves which are exhibited in Diagram IV. for iron, and Diagrams VI. and VII. for nickel, trace the change of intensity for rising temperatures; the curves for falling temperatures are not plotted, but they are nearly the same, except that in iron they are smoother, the droop which occurs between  $800^{\circ}$  and  $900^{\circ}$  A. being less pronounced.

With nickel the curves are smooth and nearly coincident for heating and cooling.

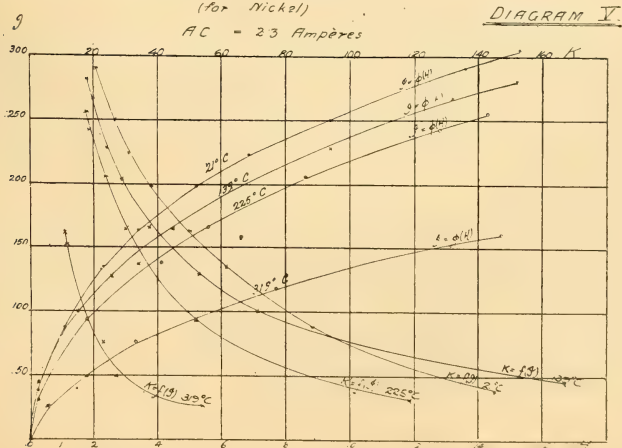
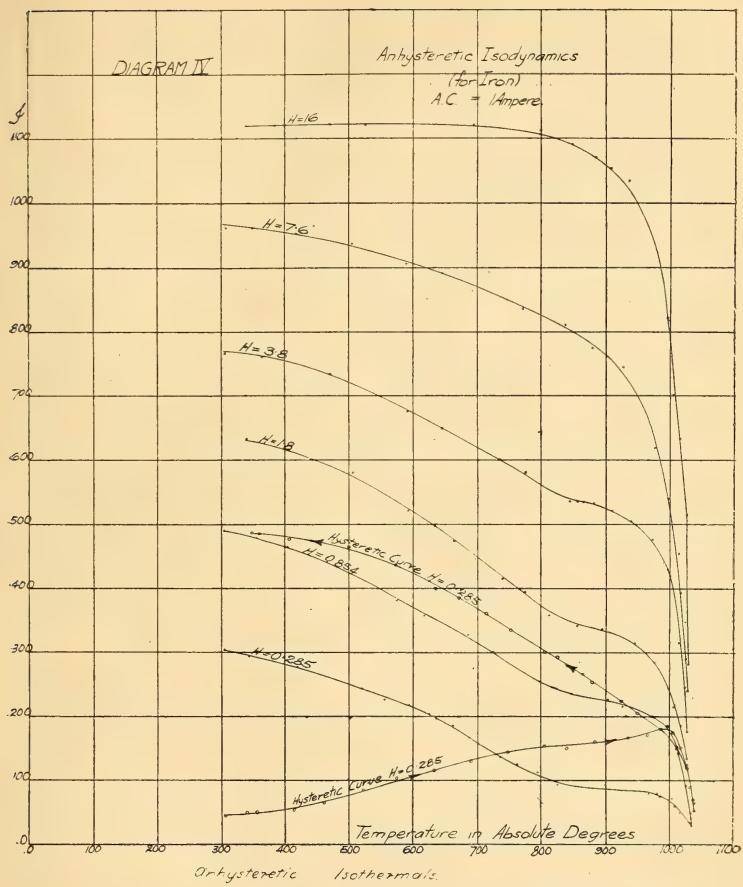
\* The crossing of the nickel curves of susceptibility for temperatures  $21^{\circ}$  C. and  $139^{\circ}$  C. shows that hysteresis is not completely suppressed.



On the other hand, the effect of hysteresis is strikingly shown in the initial hysteretic curve of I in a low field as the temperature is raised. Here I increases until a near approach to the critical temperature and then rapidly falls.



On cooling its path is entirely different; it has then the form rather of the anhyseretic curves, but with a larger value for I, under the same field. The paths of these hysteretic curves for iron and nickel are given in Diagrams IV. and VI. respectively.



The principal characteristics of these curves are the same for iron and nickel, but as the effects in nickel are more pronounced, and as this metal is not apparently affected by anomalous thermal disturbances as iron is, attention may be directed more particularly to the nickel curves.

A prominent feature to note is the concavity of the curves to the axis of temperature until the critical temperature is reached, when an inflexion takes place, and the curve afterwards passes outwards asymptotically. All the curves as far as the critical temperature exhibit the features which are associated with forces strongly orientating the molecular magnets. The concavity of these curves, however, always grows less as the external field diminishes, and in the curve for  $H=0.65$ , in nickel, it has nearly disappeared and the curve is almost linear for the greater part of its course.

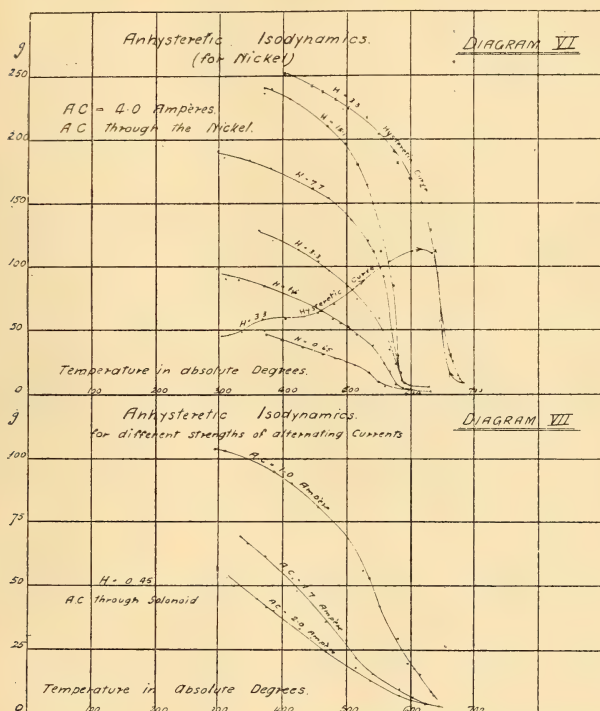
There is one feature of interest and importance which is strongly marked in this curve and is observable in the others; the convexity of the curve, which is its characteristic above the critical point, expands under low fields, and one is led to think that for a still lower field with an appropriate alternating current it might pervade the whole curve. The entire group of curves would then exhibit a gradual change from ferro-magnetic to para-magnetic properties\*.

(8) To test this view another set of experiments was arranged with this minor difference, that in this set the alternating current, instead of being led through the wire, was sent through the solenoid surrounding it, and the magnetic force acting on the nickel wire was the vertical component of the Earth's magnetism. Alternating currents of 1.0, 1.7, and 2.0 amperes were successively used, and the results which are graphed in Diagram VII. show the increasing expansion of the convex part of the curve. The curve obtained when the alternating current was 2.0 amperes is particularly interesting, as it would be difficult to fix for it a definite critical temperature. Observations (omitted from the diagram) which were taken when the alternating current was 3.0 amperes yielded a curve of similar shape to the one at 2.0 amperes.

In Diagram VI. the most prominent feature is the fact that the critical temperature can be lowered nearly  $100^{\circ}$  C. by the application of an alternating current, and it is now clear from Diagram VII. that it may be made almost indefinite.

\* A purely para-magnetic material is such that  $I$  is directly proportional to  $H$  and inversely proportional to  $T$ .

These experiments, I think, throw some light on the meaning of the critical temperature, and make it unlikely that it is due to a chemical or allotropic modification of the metal.



(9) Gerosa and Finzi\* were among the earliest to make experiments on the reduction of hysteresis by alternating current methods, and they showed that the curves so obtained can be fairly well represented by Frölich's equation. This equation may be put in the form

$$H \left( \frac{1}{I} - \frac{1}{I_0} \right) = P,$$

where  $I_0$  is the limit of magnetic intensity and  $P$  is a constant. Reducing the observations of Table I. by the

\* *Rendiconti del Reale Istituto Lombardo*, serie ii. vol. xxiv. p. 677 (1891).



method of least squares, I find the following values for the constants  $I_0$  and  $P$  for iron :—

Temperature.	$I_0$ .	$P$ .	$R' = P/T$ .
16° C. = 289° A.	933	·00132	$4.57 \times 10^{-6}$
645° C. = 918° A.	916	·00383	$4.17 \times 10^{-6}$
720° C. = 993° A.	700	·00428	$4.31 \times 10^{-6}$
776° C. = 1049° A.	511	·00600	$5.72 \times 10^{-6}$
Mean .....			$4.69 \times 10^{-6}$

If, now,  $P$  is divided by the absolute temperature  $T$ , the quotient  $R'$  is approximately constant until a near approach to the critical point. Thus the constant in Frölich's equation is proportional to the absolute temperature for these curves over a wide range of temperature. The quantity  $I_0$ , however, above 645° C. begins to diminish rather rapidly, a fact which deserves consideration. The values of  $I$  calculated from these constants are given in the third column of Table I., and comparison with the observed values allows the accuracy of the equation to be estimated.

Treating the observations on nickel in the same way, the values for the constants  $I_0$ ,  $P$ , and  $R'$  are :—

Temperature.	$I_0$ .	$P$ .	$R' = P/T$ .
21° C. = 294° A.	359	·0097	$33.1 \times 10^{-6}$
139° C. = 412° A.	333	·0109	$26.4 \times 10^{-6}$
225° C. = 498° A.	315	·0130	$26.1 \times 10^{-6}$
319° C. = 592° A.	177	·0154	$26.1 \times 10^{-6}$
Mean .....			$27.9 \times 10^{-6}$

$R'$  is again nearly constant over a considerable range of temperature; at the same time  $I_0$  diminishes as the temperature is raised. The values of  $I$  calculated from these constants are given in the third column of Table II. They show larger differences than those for iron, and indicate that the experimental curve is somewhat flatter than the calculated curve.

(10) As a first approximation the equation to the anhyseretic isothermals may be written

$$H\left(\frac{1}{I} - \frac{1}{I_0}\right) = R'T,$$

$T$  being the absolute temperature. In this form the

equation assumes a new interest. When  $I$  is very small the term  $\frac{1}{I_0}$  may be neglected and the equation then becomes

$$\frac{H}{I} = R'T \text{ or } KT = \frac{1}{R'}$$

$K$  being the susceptibility, and this is at once recognized as Curie's para-magnetic equation in which  $\frac{1}{R'}$  is the equivalent of his constant  $A$ . Comparing  $\frac{1}{R'}$ , the constant in the ferro-magnetic state, with  $A$ , we have:—

	$R'$ .	$1/R'$ .	$A$ .
Iron ... ..	$4.69 \times 10^{-6}$	$.213 \times 10^6$	.281 *
Nickel.....	$27.9 \times 10^{-6}$	$.036 \times 10^6$	.048 †
Ratio of iron to nickel .....		5.9	5.9

\* Mean value of  $A$  from experiments by Curie, *Œuvres*, p. 327, and Weiss & Foex, *Arch. des Sc.* 4<sup>e</sup> sér. t. xxxi. pp. 4, 89 (1911).

† Weiss & Bloch, *Arch. des Sc.* t. xxxiii. p. 293 (1912). (Intensity calculated as  $\frac{\text{magnetic moment}}{\text{volume}}$ .)

The absolute values of the constants are connected by a factor about  $1.33 \times 10^{-6}$ ; their ratios, however, are almost exactly the same. This perfect agreement is partly accidental, as it cannot be assumed that the iron and nickel were precisely the same in these experiments as in those with which they are compared, and that experimental errors play no part; nevertheless there is no doubt that the metals behave correspondingly ‡.

(11) If, however, the curves of  $I=f(T)$  for constant  $H$  are consulted, it is evident that the equation as it stands does not adequately represent them.

As written above it implies that  $I$  varies inversely with the absolute temperature, subject to a limiting value, and the curves should then be convex and not concave, as they are below the critical point, to the temperature axis. This concavity of the curves for large intensities at lower temperatures suggests that there is some other field of force in action, in addition to the external applied field, and it is highly probable that this is set up by the magnetization itself of the material and is some function of the intensity.

‡ See Ashworth, *Phil. Mag.* vol. xxiii. p. 36 (Jan. 1912).

The equation would then take the form

$$\left(H + f(I)\right) \left(\frac{1}{I} - \frac{1}{I_0}\right) = R'T.$$

Written thus it recalls the equation of van der Waals for fluids, field strength and magnetic intensity here playing the part of pressure and density.

(12) In conclusion, it is of interest to compare the equation obtained in paragraph (5) and the curves giving the relation of  $I$  and  $H$  to the strength of the alternating current running through the material with the equation and curves giving the relation of  $I$  and  $H$  to temperature discussed in paragraphs (9) and (10). Above a critical value of the alternating current the intensity of magnetization tends to become inversely proportional to the strength of the current, subject to a limit to the intensity. Below the critical value of the current the curves of intensity have a part less inclined to the horizontal, which suggests that there are other magnetic forces in action within the material besides that immediately due to the external field.

More generally since the effects of temperature on magnetism are like those due to an alternating current setting up a magnetic agitation, the probability that the former are kinetic effects of thermal agitation is considerably enhanced.

I wish to thank Mr. R. P. Shaw for much gratuitous help in preliminary work and in repeating some of the experimental results in this paper.

XXXVIII. *The Properties of Selenium Blocks.*  
By G. W. WHITE, B.Sc. (University of Bristol)\*.

IT is well known that the substance selenium in a certain crystalline form possesses the peculiar property of changing its electrical resistance on exposure to light. Any device consisting of two electrodes bridged over by the selenium is commonly, but not appropriately, called a "Selenium Cell." Since in this investigation the resistance change of selenium was observed, and not the production of an E.M.F. on illumination, the term "Selenium Bridge" is preferred and will be used throughout.

\* Communicated by Dr. A. M. Tyndall.

Selenium Bridges can be divided into two groups :—

- (A) Containing preparations illuminated in a direction perpendicular to that in which the resistance is measured.
- (B) Containing preparations illuminated in a direction parallel to that in which the resistance is measured.

It has generally been supposed that the main phenomena of Selenium Bridges may be explained by the change in conductivity produced by the penetration of light to a small depth at the illuminated surface. That is, the effect of light on a bridge of the first type is to change the conductivity of one of two conductors in parallel, and on bridges of the second type, to change the conductivity of one of two conductors in series.

Thus it was anticipated that, in order to prepare an appreciably sensitive "bridge of type B," the thickness of the selenium in the direction of the incident light must be exceedingly small. For instance, the first bridge of this type, made by Uljanin \*, consisted of a thin layer of crystalline selenium between two plates of glass covered with semi-transparent metal films. Righi † covered a metal plate with selenium, and placed it with the selenium side on a sheet of wire-gauze, through which the selenium could be illuminated.

While experimenting with bridges of this type, it was found by the author that it was unnecessary to use exceedingly thin selenium films, the bridge being appreciably sensitive when the thickness was several millimetres. This unexpected phenomenon could be utilised to make a bridge capable of being used as either of the two types by suitably choosing the direction of illumination. The use of this "double bridge" was to be two-fold :—

(1) To compare the two types of bridges. This has never been performed previously owing to the peculiarities exhibited by selenium, and the consequent difficulty of obtaining two identical preparations.

A theoretical comparison was deduced from mathematical considerations by Sperling ‡, who assumed an exponential change of conductivity throughout a thin illuminated layer, and concluded that "the bridge of the first type is more sensitive than that of the second, the conditions being

\* Wied, *Ann.* xxiv. p. 241 (1838).

† *Ann. d. Phys.* xii. p. 683 (1888).

‡ 'Beiträge zur Kenntnis der Selenzellen,' Göttingen, 1908.



identical in both cases, and that this difference approaches zero as the selenium slab becomes infinitely thin."

(2) It was hoped that the results of this comparison could be used to obtain an estimate of the "effective depth of penetration of the light in selenium"; that is, supposing there were a uniform specific conductivity throughout the illuminated layer, to find how deep this layer would have to be to account for the observed change in conductivity of a selenium block on illumination. Marc (1906) estimated the value  $5 \times 10^{-5}$  mm.; from the investigation of thin selenium films. Grippenber<sup>\*</sup>g showed this value to be much too small. Brown<sup>†</sup>, assuming the identity of heat and light actions in selenium, calculated the depth of the light-affected layer to be  $1.4 \times 10^{-2}$  mm.

In the present work, the method whereby it was hoped to arrive at the "effective depth" consisted of the examination of a rectangular block of selenium, one face of which was illuminated, the conductivity being measured both in a direction perpendicular to the incident light and parallel to it; that is, the preparation was to be used as a bridge of both types. The conductivity in the first direction (bridge A) is that of two conductors in parallel, one being the illuminated layer and the other the selenium in the dark. The conductivity is therefore a function of the specific conductivity of selenium in the dark, the "effective" or "average conductivity" in the light, the "depth of penetration," and the dimensions of the block. The actual function can be easily deduced from the elementary laws of "conductors in parallel." The conductivity in the second direction (bridge B) is that of two conductors in series, and is another function of the above quantities. Now the specific conductivity of selenium in the dark and the dimensions of the bridge can be measured, and hence from the equations expressing the conductivities of the illuminated block in the two directions, the "effective depth" and "effective specific conductivity in the light" can be calculated.

#### *Experimental Arrangements and Results.*

The bridge was made by crystallizing selenium in a mould of which one side was a copper plate and the opposite side a semi-transparent film of platinum deposited on glass by "cathode disintegration." A plate A of "bakelite"—an insulator which will withstand continued heating at a high

<sup>\*</sup> *Physik. Zeit.* xiii., 1912.

<sup>†</sup> *Phys. Rev.* vol. xxxiv. p. 201 (1912).

temperature—was taken, and from it was cut a rectangular block of dimensions 10 mm.  $\times$  10 mm.  $\times$  8 mm. (as shown in fig. 1). To the sides of the plate thus cut, a copper plate B and the glass plate C carrying the thin platinum film were clamped (fig. 2). Selenium contracts considerably

Fig. 1.

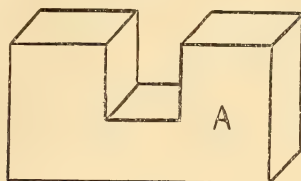
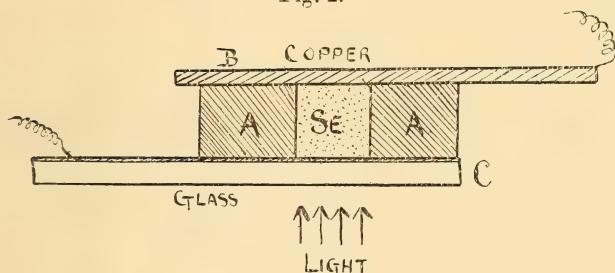


Fig. 2.



on changing from the liquid amorphous state to the crystalline, and on putting a mould containing amorphous selenium into an oven at the temperature necessary to crystallize, large cavities are formed in the selenium on solidifying. To obviate this as much as possible, in crystallizing the blocks, the following method was adopted :—Into the rectangular mould prepared as above, molten selenium was poured to a depth of about 1.5 mm. ; the mould was then kept in a hot oven until the selenium crystallized. The surface of the crystallized selenium was then melted by means of a hot steel spatula, and then molten selenium poured in to about the same depth as before and crystallized. This was repeated until the mould was full ; the whole was then kept at a temperature of about 200° C. for several days to ensure complete crystallization.

The selenium in the bridge thus prepared could be first illuminated through the platinum film (as a bridge of type B), and then the direction of the light could be changed, and the surface of the selenium exposed to the air illuminated (bridge A), the resistance in both cases being measured from the copper plate B to the platinum film C.

The resistance was always measured by means of a Post Office Box, using a fairly high voltage (4 to 20 volts) in order to make the method sensitive for such high resistances. The resistance of the illuminated bridge was observed in all cases after being illuminated for 90 seconds, and having therefore practically attained its equilibrium state.

In comparing the two types of bridges, the effect of the platinum film on the light intensity in "bridge B" was compensated for by illuminating "bridge A" by light from the same source, but which had passed through a platinum film exactly similar to that used in making the bridge.

The results of observations on three such "double bridges" are given in Table I. The selenium was illuminated by an Osram Lamp (105 v., 17 w.) at a distance of 30 cm. in cases I. and II., and at 20 cm. in case III.

TABLE I.

	Resistance measured in Direction Perpendicular to that of Light. (Bridge of Type "A.")			Resistance measured in Direction Parallel to that of Light. (Bridge of Type "B.")		
	Res. in Dark. Ohms.	Res. in Light. Ohms.	Per cent. Res. Change.	Res. in Dark. Ohms.	Res. in Light. Ohms.	Per cent. Res. Change.
I.	34,900	33,800	3.1	37,300	30,000	19.7
II.	1,110,000	1,004,000	9.6	950,000	840,000	11.5
III.	280,000	255,000	8.9	230,000	287,000	15.4

Thus with the above three bridges, the resistance change was greater when the electrode was illuminated or the bridge was used as one of type "B."

There was the possibility that this unexpected result might be due to the illumination of two different varieties of selenium, since the selenium illuminated in bridge "A" had been crystallized in contact with air, and that in bridge "B" in contact with platinum. It became necessary, therefore, not only to use the same block of selenium in both observations, *but also to illuminate the same surface*. Accordingly a cube of selenium was crystallized in a brass mould. In measuring its resistance in a direction parallel to the illumination (as bridge "B"), it was pressed between electrodes of fine copper gauze. To measure its resistance in a perpendicular direction (bridge "A"), the electrodes were removed and pressed on two other opposite faces of the cube, and the surface used in the first measurement again illuminated. As

in previous observations, the decrease in intensity of the light due to the gauze was compensated for.

With the bridges made by pressing electrodes on selenium cubes, as with those made by crystallizing selenium between copper and platinum electrodes, the same result was arrived at:—bridge "B" was invariably more sensitive than bridge "A," and calculation gave an impossible value for the "depth of penetration of the light." The results of experiments with two cubes are recorded in Table II. Illuminations of different colour were obtained by means of colour-filters (obtained from Wratten and Wainwright), the energy of the transmitted light being kept constant by using a thermopile.

TABLE II.

	Illumination.	Resistance in Direction Perpendicular to that of Light. (Bridge "A.")			Resistance in Direction Parallel to that of Light. (Bridge "B.")		
		Res. in Dark.	Res. in Light.	P. c. Res. Change.	Res. in Dark.	Res. in Light.	P. c. Res. Change.
CUBE I.	Red.....	733,000	707,000	3·6	109,400	89,500	18·2
	Green.....	732,000	717,000	2·1	104,200	93,400	10·5
	Blue .....	727,000	711,000	2·2	102,600	88,300	13·9
CUBE II.	Red.....	197,400	193,300	2·1	116,200	101,400	12·7
	Green.....	200,300	198,300	1·0	113,600	106,300	6·4
	Blue .....	203,200	200,700	1·2	109,600	99,800	8·9

It is a characteristic of selenium bridges that the resistance changes on reversing the current; but it was ascertained that, whichever way the current flowed through selenium blocks, the relatively large sensitiveness of bridge "B" showed itself. For instance, the resistance between two opposite faces of a cube was 173,000 ohms, the change on illuminating one of these faces (*i. e.* as a bridge of type "B") being 35 per cent. On reversing the current, the resistance changed to 210,000 ohms, the change on illuminating the same surface being 29 per cent. With another bridge of this type, the resistance, on reversing the current, fell from 40,000 ohms to 23,000 ohms, and the light-sensitiveness in the two directions was 45 and 23 per cent. respectively; using the preparation as a bridge of the first type, and illuminating the same surface, the resistance change never exceeded 9 per cent.



In all these observations the selenium surfaces were carefully screened from stray light, usually by an ebonite casing, and sometimes by covering the selenium surfaces which were neither used in contact with the electrodes nor illuminated by soft wax. Selenium "cells" which produced an E.M.F. in the dark or on illumination, were not used in this investigation.

A comparison of the other properties of the two types was made. A selenium cube was taken, and set up as a bridge of the second type. The increase of conductivity during illumination ("Nachwirkung"), the recovery on darkening the bridge (Trägheit), and the relation between the conductivity change and the intensity of the light were investigated. This was repeated using the same selenium cube as a bridge of the first type. The relations obtained were identical for the two types. The curves are not reproduced here, the "recovery" and "light-intensity" curves being of the usual form such as those obtained by Sperling\*, and the after-effect" curves of the same form as those obtained with a "Bidwell" bridge by Ries†.

*Discussion of Results, and other Experiments with  
Selenium Blocks.*

The above results show that with blocks of selenium, the resistance change on illumination is greater when the light is incident in the direction of the current, than when perpendicular to this direction. This is opposed to the result, referred to above, obtained theoretically by Sperling. In other words, the unexpected phenomenon revealed in the present investigation is a highly sensitive bridge of the second type, and the quantitative effect of light on bridges of both types cannot be explained by the change in conductivity in a very thin layer at the illuminated surface, the selenium block being homogeneous.

The high sensitiveness of these bridges could be accounted for, if light had the effect of decreasing the specific resistance throughout a very deep layer. Marc‡ concluded from his investigations of the "inertia" of selenium, that the action of light is far from being confined to the surface and the illuminated portion of the bridge, being transmitted all over the bridge. Brown§ suggested that the "effective depth" may be much greater than the greatest depth

\* *Loc. cit.*

† *Die elektrischen Eigenschaften des Selen.*

‡ *Zeit. Anorg. Chem.* xxxvii. 3, p. 459.

§ *Loc. cit.*

reached by the light. To account for the sensitiveness of bridge "B" often observed, the depth of selenium affected would have to be at least 2.5 mm., assuming the selenium was changed to a good conductor on illumination. This did not seem to be at all probable, but the following experiment was devised to test the possibility of the effect of light being transmitted to the dark portions of the selenium:—A block of selenium was crystallized with a sheet of fine copper gauze imbedded in it parallel to one face of the block and at a distance of 1 mm. from the surface. The opposite face of the block was pressed against a copper electrode. No change could be detected in the resistance between the imbedded gauze electrode and the copper plate electrode when the selenium surface nearest the gauze was illuminated.

Hence it appears that the resistance change on illumination occurs at the illuminated electrode. The change may be either that of a high resistance crust over the selenium block, or a "contact resistance"; other properties of selenium blocks, which will now be discussed, point to the existence of the latter.

#### *Effect of Filing the Surfaces.*

A cube was taken and the resistance between two faces measured, using copper gauze electrodes. One of these faces was rubbed carefully with a fine plane file. The author was surprised to find an increase of resistance from 520,000 to 840,000 ohms. After the second filing the resistance had increased to 1,300,000 ohms. On continuing the filing the resistance first increased slightly, and then remained fairly constant. This is a typical result of the filing of several surfaces; a marked increase was always observed at the start. The light-sensitiveness remained fairly constant during the filing, and by continuing the filing of the surface of a cube, the selenium was found to be conducting and sensitive to light throughout the whole block. This was found to be the case for Giltay "cells" by Brown\*.

The fact that filing the surface produces such a sudden and marked effect on the resistance between the electrodes, suggests that a large part of the resistance exists at the electrodes.

#### *Resistance dependent on nature of electrodes, and surface in contact with selenium during crystallization.*

The fact that the apparent resistance of selenium in the dark depends on the nature of the electrodes was first

\* *Loc. cit.*

pointed out by Graham Bell \*, and for obtaining a wire "bridge" of low resistance he recommended the use of brass in preference to platinum. The author pressed electrodes of different metals on the opposite faces of selenium cubes, and marked differences in resistance were obtained. Table III. shows the results of observations on two cubes. The direction of the current in the selenium was kept constant in the case of each cube.

TABLE III.

	Tin Foil.	Copper Foil.	Copper Gauze.
1...	21,400	74,000	98,000
2...	46,000	88,000	157,000

This fact may have its explanation in the change of the resistance at the contact of electrode and selenium.

The resistance seemed also to depend to a large extent on the nature of the mould used in crystallizing the selenium block. The light-sensitiveness of the surface also depended on this condition. For instance, the change in resistance was 25 per cent. on illuminating a wire-gauze electrode pressed on a selenium surface crystallized in contact with brass; the surface crystallized in contact with glass had a light-sensitiveness of 15 per cent. and the "air" surface 11 per cent.

The selenium blocks showed the usual characteristics of the selenium bridge, such as variation of resistance with voltage, pressure, and duration of current; and it is significant that all these properties together with that of dependence of resistance on direction of current, appear in connexion with "crystal contacts." Brown † has called attention to this similarity. It is also noteworthy that Streintz ‡ has explained the "apparent resistance" of crystals and its dependence upon the current, pressure of electrodes, temperature, &c., by the existence of a resistance at the contact of the crystal and the electrode.

Now the ordinary Bidwell wire bridges (in which the selenium is crystallized firmly on the electrodes) show the same "crystal contact" properties. Also the effect of

\* Amer. Assoc. 1880; 'Nature,' vol. xxii. p. 500.

† "The Similarity of Electrical Properties of Selenium to those in certain Crystal Contacts," Phys. Rev. 1913, p. 245.

‡ *Phys. Zeit.* 1912.

light on these bridges is identically the same as the effect on the bridges of the second type. Hence, if the effect of illuminating the electrode of the latter bridges is chiefly to change a "contact resistance," then we should expect a relatively big effect of light at the electrodes in the ordinary wire bridges. Adams and Day\* by means of a lime light and lens focussed the light on a stick of sensitive selenium, and found that "the sensitiveness was different at different parts of the same stick." Actual values of the change were not published, and the following experiment was devised by the author to obtain the variation between the electrodes. Two thin wires of phosphor-bronze were fixed parallel to one another at a distance of 15 mm. on a strip of glass of width 17 mm. the surface of which had been roughened with sand-paper. Selenium was spread over the glass between the wires, and crystallized. By means of two narrow slits a strip of selenium of width 2 mm. at any part of the bridge could be illuminated. The bridge had an initial resistance of 144,000 ohms which changed to 140,000 ohms on illuminating any strip of selenium between the electrodes, and to 134,000 ohms on illuminating either electrode. The change, therefore, was nearly three times as great at the electrode as at other points in the selenium. This receives some support from an experiment by Lindner and Replogle†, who devised a bridge consisting of selenium spread over a thin platinum film deposited on glass and scored to and fro with a fine engraving tool. To get the maximum effect on illumination, the light was admitted through the glass (illuminating the platinum electrodes). (Similar bridges were constructed and tested by the author.) Thus it appears that the action of light on bridges of both types is partly to effect a change at the contact of the electrodes with the selenium.

#### *The Crystallization of Thin Selenium Films.*

Estimates of the "depth of penetration" have been made by Grippenberg‡ from a study of thin films. Films of red amorphous selenium of thickness comparable with the wave-length of light can be obtained by "cathode disintegration." In heating the red film to convert it into the metallic light-sensitive state, investigators have encountered the difficulty that the selenium on melting forms into isolated drops giving a discontinuous film. Grippenberg‡

\* Proc. Roy. Soc. 1876, p. 113.

† 'Electrical World,' lix. p. 251 (1912).

‡ *Loc. cit.*



succeeded in obtaining continuous crystalline films by covering the amorphous film with a varnish before heating. The author attempted to crystallize the films by depositing the selenium directly on a plate placed opposite the cathode and heated by an electric current to a temperature just below the melting-point of metallic selenium. Since at that temperature amorphous selenium cannot exist, it was hoped that the particles on being deposited would be changed at once to the metallic state, and that the resulting film would be continuous and light-sensitive. It was difficult to obtain the required temperature and keep it constant, since heat was supplied to the plate from the hot cathode as well as from the heating wire; the pressure in the tube, the "cathode fall," and the strength of the heating current would therefore have an effect on the temperature of the plate. By suitably choosing the conditions, grey films were obtained which appeared crystalline and continuous; on being tested they were found to be insensitive to light, but after heating at a temperature of  $180^{\circ}\text{C}$ . for an hour, the films became sensitive to light but "light-negative" (the resistance increased on illumination). Since these results were obtained Brown\* has published work showing that light-negative selenium is produced by the action of mercury on selenium, and the property of the films obtained as above was evidently due to the presence of mercury vapour from the pump and pressure-gauge connected to the "discharge-tube." The above was repeated excluding mercury. The films obtained had a high specific resistance, and either showed a slight sensitiveness to light in a positive direction, or were practically insensitive; they became, however, much more sensitive on heating for a short time in air. The method can be applied to the construction of selenium bridges.

#### *Summary.*

(1) When a selenium block is illuminated, the resistance change in the direction of the light is appreciable even with thick blocks.

(2) This fact is utilised to prepare a selenium block the conductivity of which can be measured (*a*) in a direction parallel to the illuminated face ("bridge" of the first type), and (*b*) in a direction perpendicular to this face ("bridge" of second type).

The properties of the two types are compared.

\* Phys. Rev. vol. i. 1913, p. 237.

(3) The resistance change on illuminating a selenium block is always greater when used in a bridge of the second type. The change in conductivity throughout a thin layer at the illuminated surface of a homogeneous block is insufficient to explain this phenomenon.

(4) The effect of light on selenium blocks, the effect of filing the surfaces, and the dependence of the resistance on the nature and pressure of the electrodes, on the voltage and on certain other conditions, all point to the existence of a high resistance at the contact of the selenium and the electrodes.

(5) The action of light on all selenium bridges is to a large extent, but not wholly, to effect a change of resistance at the electrode contact.

(6) Films of selenium can be obtained by "cathode disintegration." If the deposit is received on a plate at a suitable temperature, the films are continuous and light-sensitive.

The above experiments were carried out in the Physical Laboratory of the University of Bristol under the direction of Dr. A. M. Tyndall, to whom I desire to express my best thanks for much advice and help throughout the work.

Nov. 22nd, 1913.

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XXXIX. *On Ionization and Wireless Telegraphy.*

By E. H. BARTON, D.Sc., F.R.S.E.\*

FROM the paper on the above subject by Prof. Howe †, it would appear that the relation between the theory of Dr. Eccles and some experiments recently carried out by E. H. Barton and W. B. Kilby ‡ was not made quite clear. This short note is accordingly offered in explanation.

In the work referred to no direct attempt was made to detect, either (1) any increase in velocity of wave propagation or (2) any special kind of conductivity which might be concerned with such increase. Neither was it claimed that any such effects had been sought for or detected.

The position was simply this. The theory of Eccles as to the propagation of electric waves in ionized air involved (what may be termed) an ordinary and an extraordinary effect—the first being the conductivity and the second being the increase of velocity of wave propagation. In order to test this theory experimentally, it was natural to try first if the ordinary effect (the conductivity) was

\* Communicated by the Author.

† Phil. Mag. Jan. 1914, pp. 213–215.

‡ Phil. Mag. Oct. 1913, pp. 567–578.

appreciable in air at ordinary pressures and temperatures when under electric alternations of the right order of frequency. And this was what was done. If the conductivity had been inappreciable, it would have been harder to believe in any increase of wave-velocity, since the same theory involves both effects. As the conductivity proved appreciable, it seems (to some minds at any rate) easier to believe in the increased wave-velocity under the appropriate conditions. And this is all that was claimed.

The desirability of using air at low pressures had not escaped the notice of the experimenters, and was among the matters discussed by them before starting the work \*. The line of attack then made was that which seemed best for a start, but was undertaken with the full knowledge that it by no means represented the conditions supposed to obtain in the higher regions of the atmosphere.

Any one experimental method in the laboratory will probably fall short of full correspondence with Nature in many respects, and can but throw a side light on the issue. Thus the theory of Eccles supposes long-distance *wave propagation* in air at low pressures and temperatures and ionized by the *sun*; whereas the experiments cited deal only with *oscillations* of like frequency in air under *ordinary* pressures and temperatures and ionized by *radium* or *X-rays*. Hence, the conditions of the experiments (as clearly shown in the paper) differ in three respects at least from those supposed to hold in those regions of the atmosphere to which the theory applies. Accordingly, any statement as to the experiments yielding some support to the theory should be taken in the light of the context. If isolated from the context such a statement might well appear misleading.

Probably no one piece of work can either wholly confirm or disprove such a theory as that of Eccles, but can only form one link in a chain needing other links for its completion as a conclusive confirmation or disproof.

In the meantime, if a moderate ionization produces a detectable conductivity in air at ordinary pressures and temperatures under electric oscillations of two million per second, it may well seem less difficult to suppose that the special effects needed by the theory of Eccles for ionic refraction are forthcoming under the conditions obtaining in the atmospheric regions in question.

Accordingly, in this respect and to this extent, the theory seems favoured rather than disfavoured by the experiments.

Nottingham, January 16, 1914.

\* See p. 568, Phil. Mag. Oct. 1913.



XL. *The Distribution of Scattered Röntgen Radiation.* By  
Dr. HAROLD A. WILSON, F.R.S., *Rice Institute, Houston,*  
*Texas, U.S.A.\**

EXPERIMENTS on the distribution of the Röntgen radiation scattered by elements of small atomic weight have shown that on the side of the radiator on which the primary rays are incident the intensity of the scattered rays is given approximately by the formula  $I_{\theta} = I_{90}(1 + \cos^2 \theta)$  which follows from the electromagnetic pulse theory of Röntgen rays developed by Sir J. J. Thomson. Here  $\theta$  is the angle between the scattered radiation and the incident primary radiation.

On the side of the radiator from which the primary rays emerge the scattered radiation is of much greater intensity than on the other side, especially in directions near to the emergent primary beam.

Herren Friedrich, Knipping, and Laue have recently described experiments on the diffraction of Röntgen rays by crystals †, which Laue and W. L. Bragg ‡ have shown can be explained completely by supposing that the rays are reflected by the planes in the crystal which contain a regular periodic distribution of atoms.

It is well known that metals in the solid state consist largely of small crystals arranged in an irregular manner. When Röntgen rays are scattered by a metal plate we may therefore suppose that each small crystal in the plate reflects the rays just as in the experiments of Friedrich, Knipping, and Laue. The scattered radiation from a metal plate must therefore be partly due to internal reflexion from an immense number of small crystals orientated at random and partly to scattering by the amorphous portion of the metal.

Each plane which reflects the rays in any particular crystal will occur in all the crystals with different orientations. To calculate the distribution of the scattered radiation to be expected, it is therefore only necessary to consider the way in which the intensity of the radiation from a single plane varies with its orientation.

Let the angle of incidence of the rays on a plane be  $i$  and the area of the plane be  $\alpha$ . The cross-section of the reflected beam is then  $\alpha \cos i$ . The electric intensity at a point in the reflected ray will be proportional to the number of electrons in the plane which fall inside a Fresnel's zone drawn on the

\* Communicated by the Author.

† *Sitzungsberichte der Königlich Bayerische Akademie der Wissenschaften*, June 1912.

‡ *Proc. Camb. Phil. Soc.* vol. xvii. Part 1 (1912).



plane for the point considered. The area of such a zone is inversely proportional to  $\cos i$ . Hence the energy per sq. cm. in the reflected rays is inversely proportional to  $\cos^2 i$ . The total energy in the reflected ray is therefore inversely proportional to  $\cos i$  and also directly proportional to the intensity of the radiation from a single electron. The intensity of the radiation to be expected from a body entirely composed of small crystals orientated at random is therefore, since  $\theta = 2i$ ,

$$I_{\theta} = \frac{I_0}{2} \frac{1 + \cos^2 \theta}{\cos \theta/2}.$$

When  $\theta$  is nearly equal to  $\pi$  this makes  $I_{\theta}$  very large. However, in this case the Fresnel's zones will be too large to be included in the planes in the crystals, so that the energy will not increase further after  $\theta$  reaches a value near to  $\pi$ .

Even in the amorphous parts of the metal it will be possible to draw small planes each containing a number of electrons, so that we should expect the scattered radiation from the amorphous part not to follow exactly the law  $I_{\theta} = I_{90}(1 + \cos^2 \theta)$ , but in the amorphous parts the planes will contain very few electrons, so that in most cases they will not be big enough to fill up several Fresnel's zones.

We should therefore expect to be able to represent the distribution of the scattered radiation except very near to  $\theta = \pi$  by the formula

$$I_{\theta} = A \frac{1 + \cos^2 \theta}{\cos \theta/2} + B(1 + \cos^2 \theta),$$

in which the first term represents the scattered radiation due to crystals and the second that from electrons distributed at random.

The following table gives values of  $I_{\theta}/I_{90}$  calculated by means of the equation just found and the values observed by Crowther\* for a thin plate of aluminium.

$\theta$ .	Observed.	Calculated.	
		B=0.	A=B.
0	1.8	1.4	1.7
30	1.7	1.3	1.5
60	1.4	1.0	1.1
90	1.0	1.0	1.0
120	1.8	1.8	1.6
150	3.8	4.8	3.5

\* Proc. Roy. Soc. A. vol. lxxxv. p. 40 (1911).

It appears that if we take  $A = B$  so that half the electrons are in crystals and half distributed at random, the calculated values of  $I_\theta/I_{90}$  agree fairly well with those found by Crowther.

The excess of scattered radiation in the emergence direction seems therefore to be easily explicable on the theory that Röntgen rays are very short electromagnetic waves or pulses. The only property of Röntgen rays which is not easily explicable on this theory seems to be that of causing the emission of high-velocity electrons. The most reasonable way of explaining the emission of these electrons seems to be that proposed by Planck\*, according to which matter absorbs radiant energy continuously but only emits it in definite amounts inversely proportional to the wave-length of the radiation. This view enables the ordinary electromagnetic wave theory of light and Röntgen rays to be retained.

XLI. *On Deep Water Waves.* By J. R. WILTON, M.A., B.Sc., Assistant Lecturer in Mathematics in the University of Sheffield †.

SOME time ago, when studying Stokes's papers on Oscillatory Waves (Collected Works, vol. i. and vol. v.), I noticed that the work of determining the coefficients in the expansions of the coordinates might be very considerably reduced, and that the order of magnitude of any coefficient was determinate. These expansions may, without great labour, be carried to a high order of approximation, and the form of the wave may be drawn for a value of the amplitude not far short of that for the highest wave.

By a change in the notation we are enabled to treat the progressive wave directly, and at the same time to retain all the advantages of the customary method of reducing the problem first to one of steady motion. The advantage of the change will be more apparent to anyone who attempts to discuss the stability of the wave.

We shall use throughout the abbreviations :

$$\begin{aligned} z &= x + iy, & z' &= x - iy, \\ w &= \phi + i\psi, & w' &= \phi - i\psi, \\ \eta &= \frac{2\pi}{\lambda} (ct - z), & \eta' &= \frac{2\pi}{\lambda} (ct - z'), \\ \xi &= \frac{2\pi}{\lambda} \frac{w}{c} + \eta, & \xi' &= \frac{2\pi}{\lambda} \frac{w'}{c} + \eta', \end{aligned}$$

\* *Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften*, April 3, 1913.

† Communicated by the Author.

where  $\lambda$ ,  $c$ ,  $\phi$ , and  $\psi$  are the wave-length, wave velocity, velocity potential, and current function, respectively.

We assume that  $\eta$  is a function of  $\xi$ , say,

$$\eta = F(\xi). \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The conditions which have to be satisfied are  $w=0$  when  $y=\infty$ ; and, on the free surface,  $y=f(ct-x)$ ,

$$\frac{\partial f}{\partial x}(c-u)=v,$$

$$\dot{\phi} + \frac{1}{2}q^2 = gy - \frac{1}{2}C',$$

where  $u$  and  $v$  are, respectively, the horizontal and vertical velocities, and  $q$  is the resultant velocity. The axis of  $y$  is vertically downwards, that of  $x$  horizontal. We shall also take the origin at the trough of a wave when  $t=0$ .

The first of the two surface conditions is satisfied whatever the form of the function  $F$ , provided that  $\xi$  is real on the surface, *i. e.* if

$$\psi = cy$$

on the surface.

Let

$$\eta' = F'(\xi') \quad . \quad . \quad . \quad . \quad . \quad (2)$$

be the equation obtained from (1) by changing the sign of  $\epsilon$  throughout. We then have

$$u - v = \frac{dw}{dz},$$

$$\frac{d\eta}{d\xi} \left( \frac{dw}{dz} - c \right) = -c,$$

or

$$c - u + v = c \left/ \frac{d\eta}{d\xi} \right.$$

and

$$c - u - v = c \left/ \frac{d\eta'}{d\xi'} \right.$$

Also

$$c = \frac{\lambda}{2\pi} \frac{\partial \eta}{\partial t} = \frac{d\eta}{d\xi} \left( \frac{\dot{\phi} + v\dot{\psi}}{c} + c \right),$$

*i. e.*

$$\frac{\dot{\phi} + v\dot{\psi}}{c} = -c + c \left/ \frac{d\eta}{d\xi} \right. = -(u - v),$$

$$\frac{\dot{\phi} - v\dot{\psi}}{c} = -(u + v);$$

therefore

$$\dot{\phi} = -uc,$$

so that the condition of constant pressure on the free surface becomes

$$(c - u)^2 + v^2 = c^2 - C' + 2gy,$$

*i. e.*

$$\frac{1}{\frac{d\eta}{d\xi} \frac{d\eta'}{d\xi'}} = \frac{g\lambda}{2\pi c^2} [\iota(\eta - \eta') - 2C]. \quad (3)$$

We must, further, have  $w=0$ , *i. e.*  $\eta=\xi$ , when  $y=\infty$ , or  $\xi=-\iota\infty$ . This condition is satisfied if we assume the expansion

$$\eta = \xi + \iota A_1 e^{-\iota\xi} + \iota A_2 e^{-2\iota\xi} + \dots$$

as the form of  $\eta^*$ . Making the assumption, and substituting in equation (3), we find, as the equation to determine the coefficients  $A_n$ ,

$$0 = \frac{\pi c^2}{g\lambda} + \left[ C + \sum_{n=1}^{\infty} A_n \cos n\xi \right] \left[ \left( 1 + \sum_{n=1}^{\infty} n A_n \cos n\xi \right)^2 + \left( \sum_{n=1}^{\infty} n A_n \sin n\xi \right)^2 \right].$$

The terms of this equation must be re-arranged in cosines of multiples of  $\xi$ , and then the coefficient of each cosine is to be equated to zero. The general form of the equations so

\* I find it difficult to persuade myself that this is the *only* form of  $F$ . It is possible, if we do not make this assumption, to satisfy equation (3), together with the condition of rest at the bottom of the liquid, in an infinite number of ways, and in certain cases the exact expression for the function  $F$  may be obtained. In fact if we put  $\eta = \eta_1 + \iota\eta_2$ , where  $\eta_1$  and  $\eta_2$  are real when  $\xi$  is real, equation (3) is satisfied provided that

$$\eta_1 = \int \sqrt{-\frac{\pi c^2}{g\lambda(C + \eta_2)} - \eta_2'^2} d\xi;$$

and the only remaining condition is that  $\eta = \xi$ , when  $\xi = -\iota\infty$ . A function satisfying this condition is that given by the equation

$$\eta_2 e^{\frac{g\lambda}{\pi c^2} \eta_2} = A \cos \frac{g\lambda}{2\pi c^2} \xi,$$

which presents some remarkable points of resemblance to Stokes's wave. Such "waves" are, however, not in general such that the crests of all the stream-lines are vertically under the crests of the free surface. Stokes's solution is the only one which satisfies this condition.

The wave considered in the paper "On the Highest Wave in Deep Water" (Phil. Mag. Dec. 1913, pp. 1053-8) is of the type considered in this note. Another example, perhaps even more curious, is that of the steady motion represented by the equations

$$\frac{g^2}{c^2} = \theta + \iota - \iota^3,$$

$$\frac{gw}{2c^3} = \theta + \sin \theta,$$

in which the complete cycloid obtained by making  $\theta$  a real quantity is a free surface, for which  $\psi=0$ . The fluid is, moreover, at rest at the bottom, where  $y=-\infty$ ,  $\theta=-\iota\infty$ . In this case there is no need, as in the paper referred to, to "fit on" various distinct arcs of the complete curve.



obtained is as follows :—

$$\begin{aligned}
 0 &= \frac{\pi c^2}{g\lambda} + C \left( 1 + \sum_{n=1}^{\infty} n^2 A_n^2 \right) + \sum_{n=1}^{\infty} n A_n^2 + \sum_{n=1}^{\infty} A_n \sum_{m=1}^{\infty} m(m+n) A_m A_{m+n}, \\
 0 &= C \left[ 2r A_r + 2 \sum_{m=1}^{\infty} m(m+r) A_m A_{m+r} \right] + A_r + \sum_{n=1}^{\infty} (2n+r) A_n A_{n+r} \\
 &\quad + \frac{1}{2} \sum_{n=1}^{r-1} r A_n A_{r-n} + \sum_{n=1}^{\infty} A_n \sum_{m=1}^{\infty} m(m+n+r) A_m A_{m+n+r} \\
 &\quad + \sum_{n=1}^{\infty} A_n \sum_{m=1}^{\infty} m(m+n-r) A_m A_{m+n-r},
 \end{aligned}$$

for all values of  $r$  from 1 to infinity. It is understood that in the last summation  $m+n-r$  is positive.

These equations must be solved by a process of successive approximation. The equations, to any desired order, may be written down from the above general expression, or by means of a rule derived from it. The rule, which is somewhat complicated, is as follows :—

The equation obtained by equating the coefficient of  $\cos p\xi$  to zero is made up of terms :

(1)  $C$  multiplied by

$$2pA_p + 2(p+1)A_1A_{p+1} + 4(p+2)A_2A_{p+2} + \&c.$$

(2)  $A_p$ .

(3) All terms made up of the product of two coefficients the sum or difference of whose subscripts is  $p$ ; and the numerical multiplier of any term is the sum of the subscripts unless the term is a square, in which case it must be halved.

(4) All terms made up of the product of three coefficients whose subscripts are such that the sum of two of them minus the third is  $\pm p$ ; and the numerical multiplier of any term is the product of the two numbers whose difference is  $p$  and whose sum is the sum of the subscripts of the coefficients forming the term. If, however, one of the terms contains the square of a coefficient, and is such that twice the subscript of this term minus the subscript of the remaining coefficient is  $\pm p$ , the term is to be halved, but not otherwise.

As an example of the use of the rule, the equation for which  $p=2$  is here written down to the twelfth order. It is

$$\begin{aligned}
 0 &= C(4A_2 + 6A_1A_3 + 16A_2A_4 + 30A_3A_5 + 48A_4A_6 + 70A_5A_7) \\
 &\quad + A_2 + A_1^2 + 3A_1^2A_2 + 4A_1A_3 + 8A_1A_2A_3 + 4A_1^2A_4 + 4A_2^3 \\
 &\quad + 6A_2A_4 + 15A_1A_3A_4 + 15A_1A_2A_5 + 15A_2A_3^2 + 8A_3A_5 \\
 &\quad + 24A_1A_4A_5 + 24A_1A_3A_6 + 24A_2A_4^2 + 12A_2^2A_6 + 12A_3^2A_4 \\
 &\quad + 10A_1A_6 + 35A_1A_5A_6 + 35A_1A_4A_7 + 35A_2A_5^2 \\
 &\quad + 35A_2A_3A_7 + 35A_3A_4A_5 + 12A_5A_7 + 6A_6^2.
 \end{aligned}$$

The leading term in each coefficient  $A_n$  may be written down. In fact,

$$A_n = (-)^n \frac{n^{n-2} a^n}{(n-1)!} + \text{higher powers of } a,$$

where  $A_1 = -a$ .

For, if we retain only the first approximation to each coefficient, we shall have, in order to determine  $A_n$  from the values of  $A_1, A_2 \dots A_{n-1}$ , supposed known, the equation

$$(n-1)A_n = n(A_1 A_{n-1} + A_2 A_{n-2} + A_3 A_{n-3} + \dots),$$

where the last term on the right-hand side is  $\frac{1}{2} A_{\frac{3}{2}n}^2$  if  $n$  is even, and  $A_{\frac{n-1}{2}} A_{\frac{n+1}{2}}$  if  $n$  is odd. We have also put  $C = -\frac{1}{2}$ , its approximate value.

The solution of this system of equations is easily seen to be, assuming  $A_1 = -a$ ,

$$A_n = (-)^n \frac{n^{n-2} a^n}{(n-1)!}.$$

The most direct proof is obtained by expanding  $x$  and  $x^2$  in powers of  $ae^x$  by Burmann's theorem, squaring the first result, and comparing with the second.

I have not been able to find a general formula for even the second order approximation to the value of  $A_n$ . It is, however, easy to derive a sequence formula by means of which the second order approximation to any given coefficient may be calculated. In fact, if we retain terms of order  $r+2$  in the equation for  $A_r$ , we obtain

$$C[2rA_r + 2(r+1)A_1A_{r+1}] + A_r + \frac{1}{2}r(A_1A_{r-1} + A_2A_{r-2} + \dots A_{r-1}A_1) + A_1[rA_1A_r + (r-1)A_2A_{r-1} + \dots A_rA_1] = 0,$$

i. e.

$$(r-1)A_r - \frac{1}{2}r(A_1A_{r-1} + A_2A_{r-2} + \dots A_{r-1}A_1) + 2ra^2A_r - (r+1)A_1A_{r+1} = 0.$$

If we put

$$(-)^r A_r = \frac{r^{r-2} a^r}{(r-1)!} + B_r a^{r+2},$$

we obtain the following sequence equation for  $B_r$  :—

$$(r-1)B_r - r[B_{r-1} + B_{r-2} + \frac{3}{2}B_{r-3} + \frac{8}{3}B_{r-4} + \dots + \frac{(r-2)^{r-4}}{(r-3)!}B_2] = \frac{1}{r!} [(r+1)^r - 2r^r].$$

In the same way, if we put

$$(-)^r A_r = \frac{r^{r-2} a^r}{(r-1)!} + B_r a^{r+2} + C_r a^{r+4},$$

we shall find the following sequence equation for  $C_r$  :—

$$\begin{aligned} (r-1)C_r - r \left[ C_{r-1} + C_{r-2} + \frac{3}{2} C_{r-3} + \frac{8}{3} C_{r-4} + \dots \right] \\ = (r+1)B_{r+1} + \frac{1}{(r+1)!} (r+2)^{r+1} + r \left[ B_2 B_{r-2} + B_3 B_{r-3} + \dots \right. \\ \left. + \frac{1}{2} B_{\frac{3}{2}r}^2 \left( \text{or } B_{\frac{r-1}{2}} B_{\frac{r+1}{2}} \right) \right] - 2rB_r - \frac{11}{2} \frac{r^{r-1}}{(r-1)!}. \end{aligned}$$

The corresponding sequence equations for the higher approximations become exceedingly complicated in form.

I find to the eighth order the following values of the coefficients :—

$$A_1 = -a,$$

$$A_2 = a^2 + \frac{1}{2}a^4 + \frac{29}{12}a^6 + \frac{1123}{72}a^8,$$

$$A_3 = -\left( \frac{3}{2}a^3 + \frac{19}{12}a^5 + \frac{1183}{144}a^7 \right),$$

$$A_4 = \frac{8}{3}a^4 + \frac{313}{72}a^6 + \frac{103727}{4320}a^8,$$

$$A_5 = -\left( \frac{125}{24}a^5 + \frac{16603}{1440}a^7 \right),$$

$$A_6 = \frac{54}{5}a^6 + \frac{54473}{1800}a^8,$$

$$A_7 = -\frac{7^5}{6!}a^7,$$

$$A_8 = \frac{8^6}{7!}a^8,$$

$$C = -\left( \frac{1}{2} + a^2 + \frac{11}{4}a^4 + \frac{167}{12}a^6 + \frac{29893}{288}a^8 \right),$$

$$\frac{2\pi c^2}{g\lambda} = 1 + a^2 + \frac{7}{2}a^4 + \frac{229}{12}a^6 + \frac{7427}{48}a^8,$$

and to the tenth order—

$$-A_1 = a,$$

$$A_2 = a^2 + \cdot 5a^4 + 2\cdot 417a^6 + 15\cdot 597a^8 + 64\cdot 08a^{10},$$

$$-A_3 = 1\cdot 5a^3 + 1\cdot 583a^5 + 8\cdot 215a^7 + 55\cdot 01a^9,$$

$$A_4 = 2\cdot 667a^4 + 4\cdot 347a^6 + 24\cdot 01a^8 + 166\cdot 2a^{10},$$

$$-A_5 = 5\cdot 208a^5 + 11\cdot 53a^7 + 67\cdot 40a^9,$$

$$A_6 = 10\cdot 8a^6 + 30\cdot 26a^8 + 186\cdot 5a^{10},$$

$$-A_7 = 23 \cdot 34a^7 + 79 \cdot 20a^9 + 498 \cdot 3a^{11},$$

$$A_8 = 52 \cdot 01a^8 + 207 \cdot 4a^{10} + 1390a^{12},$$

$$-A_9 = 118 \cdot 6a^9 + 543 \cdot 4a^{11},$$

$$A_{10} = 275 \cdot 6a^{10} + 1426a^{12},$$

$$-A_{11} = 649 \cdot 8a^{11},$$

$$A_{12} = 1551a^{12},$$

$$-C = \cdot 5 + a^2 + 2 \cdot 75a^4 + 13 \cdot 92a^6 + 103 \cdot 8a^8 + 823 \cdot 8a^{10},$$

$$\frac{2\pi c^2}{g\lambda} = 1 + a^2 + 3 \cdot 5a^4 + 19 \cdot 08a^6 + 154 \cdot 7a^8 + 1297a^{10}.$$

The series for  $\eta$  certainly becomes divergent in the neighbourhood of the crest of the wave when  $a$  is greater than  $1/e$ , where  $e$  is the base of natural logarithms, and the differential coefficients which occur in equation (3) become divergent when  $a=1/e$ . For the series formed by the leading terms of the various coefficients is

$$\sum_{m=1}^{\infty} \frac{m^{m-2}a^m}{(m-1)!},$$

and this is divergent when  $a$  is greater than  $1/e$ , though it converges when  $a=1/e$ . For when  $m$  is large the  $m$ th term of this series is

$$\begin{aligned} & m^{m-2}a^m e^{m-1} \left/ \left\{ \sqrt{2\pi} (m-1)^{m-\frac{1}{2}} \right\} \right. \\ &= a^m (m-1)^{\frac{1}{2}} e^m \left/ \left\{ \sqrt{2\pi} e \left(1 - \frac{1}{m}\right)^m m^2 \right\} \right. \\ &= (ae)^m m^{-\frac{3}{2}} \left/ \sqrt{2\pi} \right., \end{aligned}$$

which proves the desired result. Further, the corresponding term of the series for  $\frac{d\eta}{d\xi}$  is of order  $(ae)^m m^{-\frac{1}{2}}$ , so that this series diverges when  $a=1/e$ . Both series are, however, convergent when  $a < 1/e$ .

Moreover, the terms of any one coefficient are all of the same sign, so that the divergence of the series when  $a$  is greater than  $1/e$  is increased by the presence of these terms, and its convergence when  $a$  is less than  $1/e$  is rendered doubtful. It is impossible, with the numbers given above, to say with any certainty whether the series for any given coefficient is convergent or not, but the general impression is that all become divergent when  $a=1/3$  or thereabouts.



For  $a=1/\sqrt{10}$ , I find :—

$$\begin{array}{lll} -A_1 = \cdot 316, & -A_5 = \cdot 026, & -A_9 = \cdot 006, \\ A_2 = \cdot 112, & A_6 = \cdot 019, & A_{10} = \cdot 004, \\ -A_3 = \cdot 060, & -A_7 = \cdot 013, & -A_{11} = \cdot 003, \\ A_4 = \cdot 037, & A_8 = \cdot 010, & A_{12} = \cdot 002, \\ \frac{2\pi A}{\lambda} = \cdot 86, & \lambda/A = 7\cdot 3, & \frac{2\pi c^2}{g\lambda} = 1\cdot 2, \end{array}$$

where  $A$  is the amplitude of the wave. Comparison of these figures with those obtained by Michell\* for the corresponding quantities in the case of the highest wave show that the wave for which  $a=1/\sqrt{10}$  is not far short of the highest. Michell's figures are

$$\lambda/A = 7\cdot 04, \quad \frac{2\pi c^2}{g\lambda} = 1\cdot 20.$$

From the above values of the coefficients I find the following table of values of  $ct-x$  and  $y$  on the free surface, whose equation, given by putting  $\psi=cy$  in the expression for  $\eta$  as a function of  $\xi$  and then equating real and imaginary parts, is found to be that resulting from the elimination of  $\xi$

$$\left( \xi = \frac{2\pi}{\lambda c} \{ \phi + c(ct-x) \} \right)$$

between

$$\frac{2\pi}{\lambda} (ct-x) = \xi + A_1 \sin \xi + A_2 \sin 2\xi + \dots$$

and

$$-\frac{2\pi y}{\lambda} = A_1 \cos \xi + A_2 \cos 2\xi + \dots$$

$\xi$ .	$\frac{2\pi}{\lambda} (ct-x)$ .	$\frac{2\pi}{\lambda} y$ .	$\xi$ .
0°	0	·24	360°
45°	·64	·20	315°
90°	1·30	·09	270°
135°	2·01	—·13	225°
150°	2·28	—·26	210°
165°	2·60	—·42	195°
170°	2·75	—·53	190°
175°	2·93	—·59	185°
180°	3·14	—·62	180°

\* Phil. Mag. November 1893.

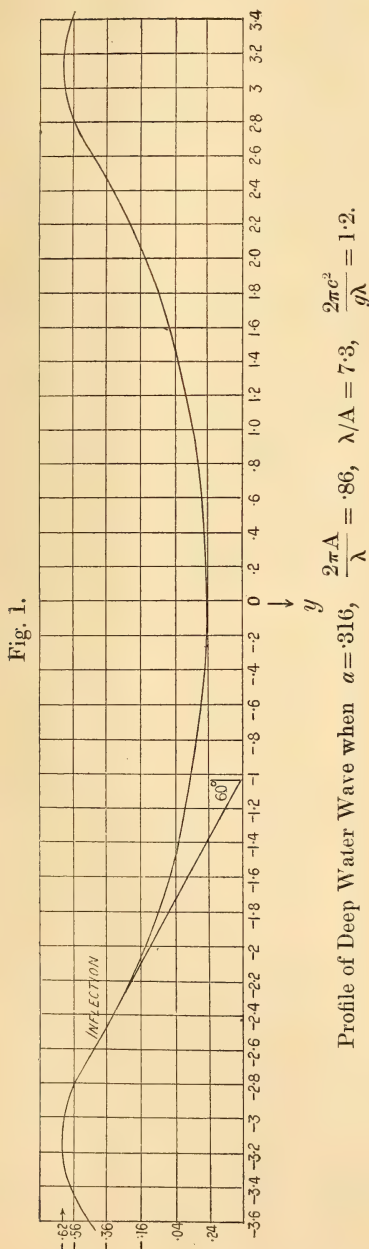
The curve obtained from these numbers is shown in fig. 1. It will be seen that the point of inflexion is very much

nearer to the crest of the wave than to the trough, and that the greatest slope of the wave is, as nearly as can be measured,  $30^\circ$ . This is just what it should be at the crest of the highest wave.

There can be no doubt that Stokes's series become, as he supposed, divergent in the neighbourhood of the crest of the highest wave, but they evidently hold right up to this point.

I have also attempted to determine whether the wave-profile becomes unstable for a ratio of amplitude to wavelength less than that for the highest wave, but as the work is laborious, and the conclusion arrived at is the merely negative one that, so far as it is possible to tell from the somewhat imperfect analysis, it does not become exponentially unstable until  $a$  exceeds the value corresponding to the highest wave for which Stokes's series converge, I have not included it.

In attempting to determine the stability of the wave, we are compelled to consider only a small disturbance of the progressive wave profile, depending on a time-factor of the form  $e^{-kt}$ , where  $k$  may be complex. We are also compelled, in order to prevent the analysis from becoming unmanageable, to assume that  $a^4$  is



negligible. The first supposition is the one which is always made, although it may on occasion lead to difficulty, as, for example, in the case of the flow of viscous fluid between two parallel planes which, as is well known, is mathematically stable for small disturbances, but is experimentally unstable if the velocity exceeds a certain value. If the real part of  $k$  had been negative, the wave would necessarily have been unstable; but, although it is actually zero, it is not therefore absolutely certain that the wave is stable.

The second supposition, that  $a^4$  is negligible, may be justified by the considerations that  $a^2$  does not exceed one-tenth, and that in the final equation which is found for  $k$  the coefficient of  $a^2$  ( $a$  does not occur to any odd power in this equation) is of the same order of magnitude as the term independent of  $a$ .

**XLII.** *On the Number of Ions produced by the Gamma Radiation from Radium.* By A. S. EVE, D.Sc., Macdonald Professor of Physics, McGill University, Montreal\*.

**I**F  $q$  ions are produced, directly or indirectly, in a cubic centimetre of air, at standard temperature and pressure, at a distance of  $r$  cm. from a source of  $Q$  gm. of radium, then

$$q = KQ/r^2 e^{\mu r},$$

where  $K$  is a constant, and  $\mu$  is the coefficient of absorption of the  $\gamma$  rays in air.

Also the total number of ions produced in air by the  $\gamma$  rays from  $Q$  gm. will be found by integration to be

$$N = 4\pi KQ/\mu.$$

The first determination† of  $K$  was made in 1906 with an aluminium vessel, 0.4 mm. thick, and for radium bromide, assuming  $e = 3.4 \times 10^{-10}$ , the value was  $3.1 \times 10^9$ . This is equivalent to  $K = 3.8 \times 10^9$  for a gramme of radium with  $e = 4.7 \times 10^{-10}$ .

The second and third determinations‡, made in 1911, with very thin-walled testing vessels, gave values  $K = 3.74 \times 10^9$  and  $3.81 \times 10^9$  respectively. Accepting Chadwick's value for  $\mu$  as .000060 the corresponding value of  $N$  is  $7.8 \times 10^{14}$ .

In Rutherford's 'Radioactive Substances' (1913), p. 295, it is stated that Moseley and Robinson have found  $N = 13 \times 10^{14}$ . This corresponds to  $K = 6.2 \times 10^9$ , a value

\* Communicated by the Author.

† Phil. Mag. September 1906.

‡ Phil. Mag. October 1911.

which is more than 60 per cent. higher than the mean of the three above determinations. As no account of the experiments of Moseley and Robinson has been published, up to the time of writing this note, it is premature to make any suggestions as to the explanation of the divergence of values, but it seems surprising that there should be so large a discrepancy for a constant which should surely be known within a few per cent.

The matter is of some importance inasmuch as the constant  $K$  enters into the calculation of the ionization energy of the  $\gamma$  radiation, and the consequent heating effect due to  $\gamma$  rays.

Moreover, L. V. King\* has used Moseley and Robinson's value ( $N=13 \times 10^{14}$  ions, leading to  $K=6 \times 10^9$ ) in his estimate of the calculated diminution of the penetrating radiation, due to radioactive matter in the earth, with increase of altitude above the earth's surface. The diminution with altitude as determined by Gockel and Hess† during balloon flights is not in good agreement with the calculated variation, but it is not suggested that the discrepancy has anything to do with the value assigned to  $K$ . Hess has determined the values of this constant for the testing vessels and Wulf electrometers used in his balloon voyages, and the values found for  $K$ , for the ionization within the vessels, are  $5.67 \times 10^{-9}$ , and  $4.87 \times 10^{-9}$ . The materials of his testing vessels do not appear to be stated in his paper, but assuming them to be brass or copper or zinc, the corresponding values for  $K$  in air‡ would be about  $4 \times 10^9$  and  $3.5 \times 10^9$ , which are in fair agreement with my values.

The writer has just made a fresh determination of  $K$  with a thin cardboard testing vessel, lightly coated inside with lamp-black, on a Wulf electrometer, and found  $K=3.8 \times 10^9$ , in good agreement with his three previous determinations.

It is possible that the determinations of Moseley and Robinson were made with radium emanation and active deposit contained in a thin-walled glass vessel, and that consequently their value of  $N(13 \times 10^{14})$  included the ions produced by the softer radiations attributed to radium B§.

It must be remembered that the values for  $K$  given above by the writer do not include the ionization due to these easily absorbed rays.

For the purpose of calculation of the atmospheric ionization, due to radium and its equilibrium products in the earth,

\* Phil. Mag. October 1913.

† *Phys. Zeit.* xiv. p. 614 (1913).

‡ Phil. Mag. September 1912.

§ Moseley & Robinson, Phil. Mag. xxiii. p. 312 (1912). Rutherford & Richardson, Phil. Mag. May 1913.



the value of  $K$  should probably be taken as  $3.8 \times 10^9$ , as the greater part of the soft  $\gamma$  radiation due to radium B would not pass from the earth, but undergo absorption in the soil.

On the other hand, if the heating effect of the  $\gamma$  radiation from radium and its products is to be calculated from the resulting ionization, then obviously the effects of all the soft  $\gamma$  radiation should be included, and the whole calculation becomes a difficult one.

An addition of about five per cent. should be made to the above figures if the International radium standard be adopted, so that then  $K = 4.0 \times 10^9$  and  $N = 8.4 \times 10^{14}$ .

#### *Summary.*

A redetermination has been made of the total number of ions which can be produced in air by the  $\gamma$  rays from a gramme of radium and its subsequent products. The number found is  $8.4 \times 10^{14}$ , in close agreement with previous determinations, but the value does not include the number produced by the easily absorbed  $\gamma$  rays.

#### *XLIII. Notices respecting New Books.*

*Annals of the Astrophysical Observatory of the Smithsonian Institution.*

Volume III. By C. G. ABBOT, Director, F. E. FOWLE and L. B. ALDRICH. Quarto. Pp. xi+241. Washington, 1913.

**T**HIS volume gives a survey of the operations of the Smithsonian Institution directed towards the determination of the "Solar constant of radiation" since July 1907. Extensive observations have been made at Washington, on Mount Wilson and Mount Whitney, both in California, and at Bassour, Algeria. The volume describes in detail the instruments, pyrheliometers and bolometers of various types, explains the processes of reduction adopted, and gives tables of results. The combination of observations from nearly sea-level at Washington, 5700 feet on Mount Wilson, and 14500 feet on Mount Whitney, affords a check on the corrections applied for absorption by the earth's atmosphere; while the comparison of American and Algerian results enables conclusions to be drawn as to the general character of the phenomena. It is claimed that the scale of measurement of radiation and the value of the "solar constant" of radiation have been established to within 1 per cent. For the "solar constant" the mean value derived from the observation of the 11 years 1902-1912 is 1.932 calories per sq. cm. per minute. The conclusion is, however, drawn that the sun's radiation is not really constant, "but varies, with an irregular periodicity of from 7 to 10 days on the average, and with irregular amounts seldom if ever exceeding 10 per cent." This is a result of such far reaching importance that confirmation from an absolutely independent source will probably be found necessary to secure universal acceptance

CLARINET.

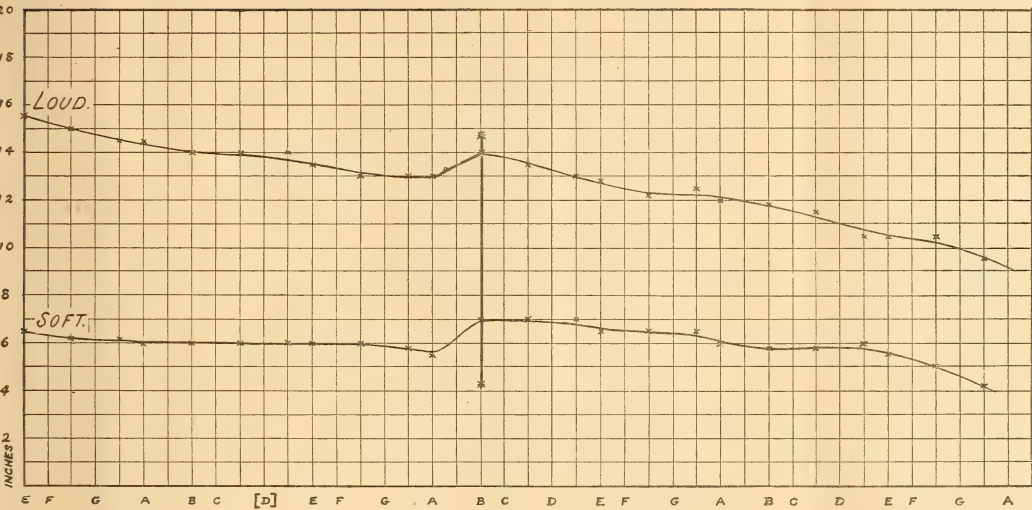


FIG. 1.

E<sup>b</sup> SAXOPHONE.

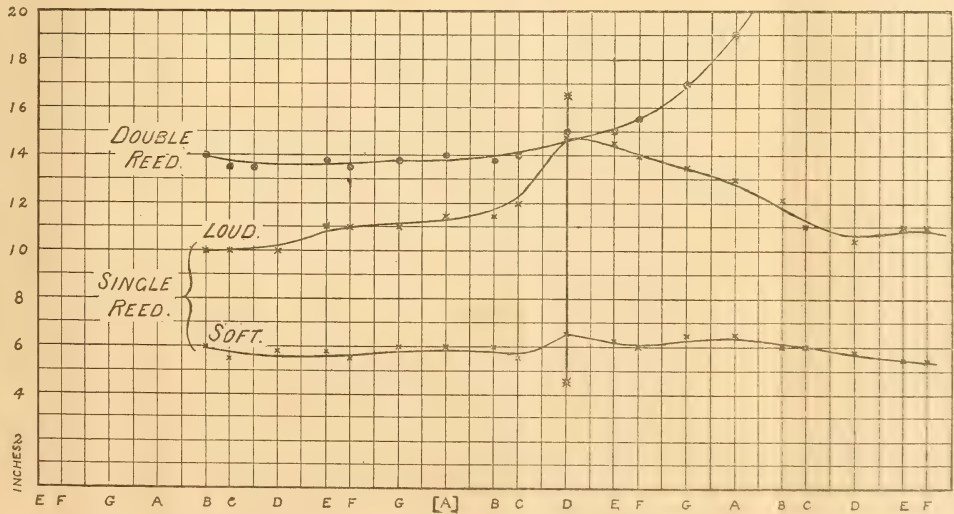


FIG. 2.



.0000

.0000

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-1.0

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-1.7

-1.2

190

170

150

130

110

90

70

50

30

10

0

-2

-4

-6

-8

VISCOSITY

80

70

60

VISCOSITY

DENSITY

1.0

1.05

1.1

1.15

1.2

1.25

DENSITY-VISCOSITY CURVE

for

AMMONIUM NITRATE $T = 10^{\circ}C$ 

Minimum Viscosity = 65

 $x = 1.0825$ GRAPH of  $\log(P-x)$  and  $\log(1-\frac{x}{\mu})$ for AMMONIUM NITRATE andMANGANESE CHLORIDE

MIN. 103

 $x = 1.0825$  $\log(1-\frac{x}{\mu})$ 

4

2

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-4

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-8

-10

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-18

-20

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-28

-30

-32

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Fig. 2.

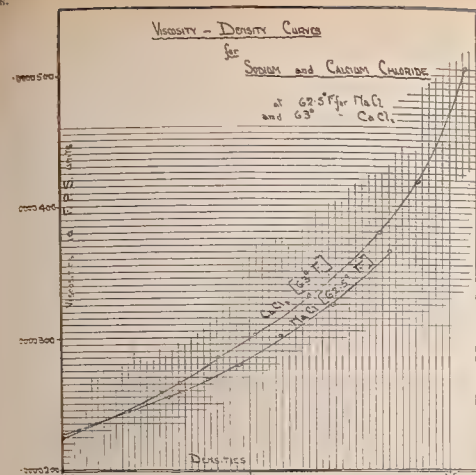


Fig. 3.

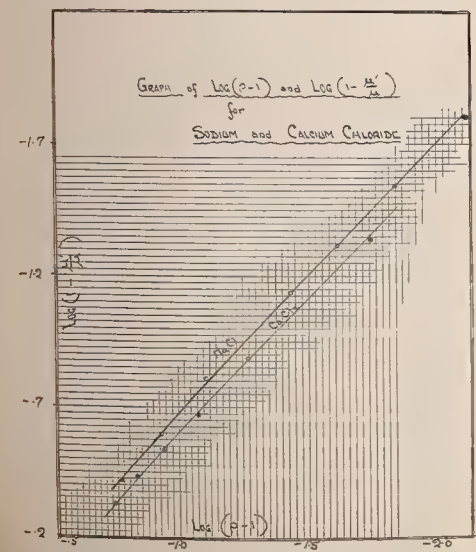


Fig. 5.

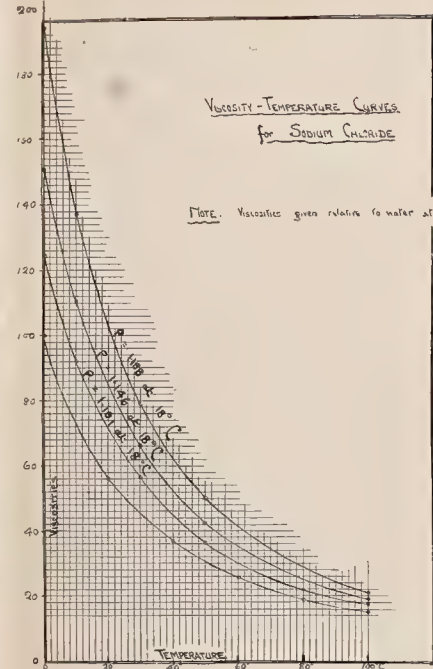


Fig. 6.

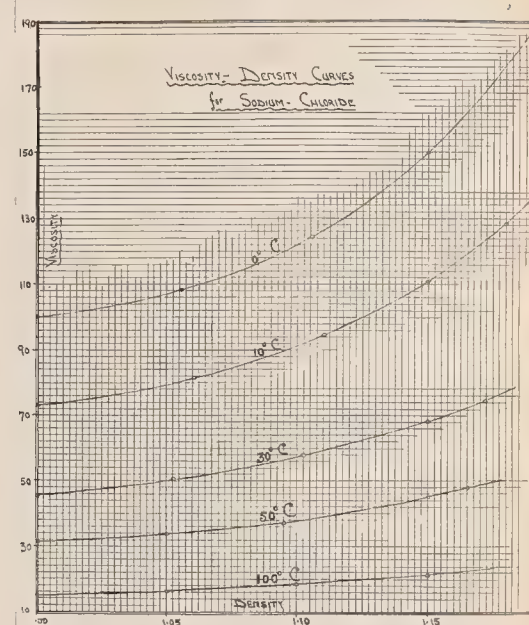


Fig. 7.

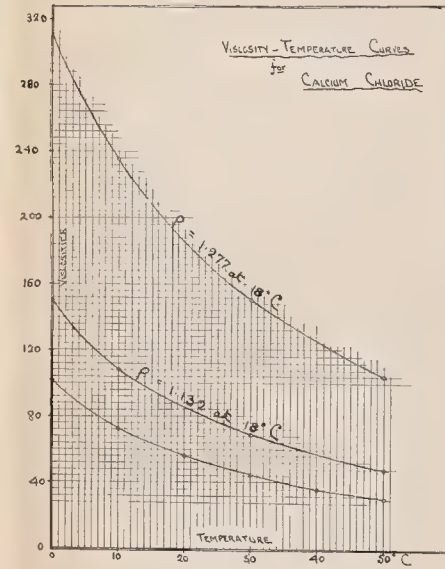


Fig. 8.

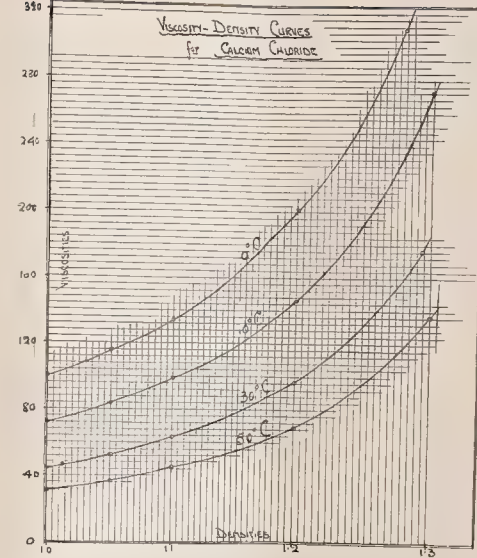


Fig. 9.

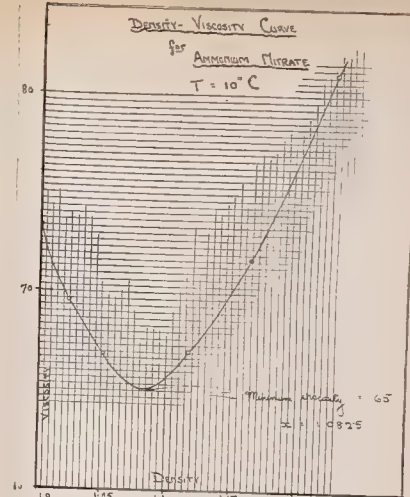
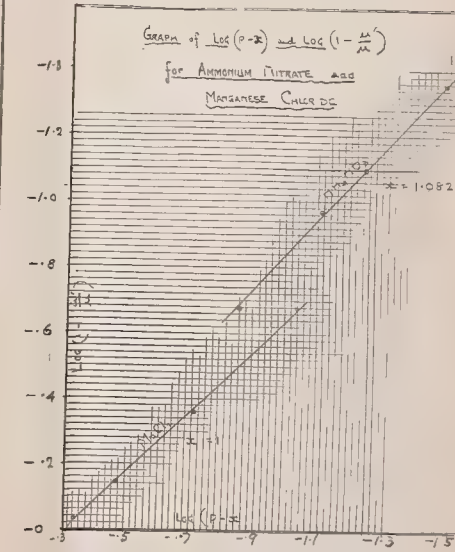


Fig. 10.





5461

(p)

Fig. 7.

(s)

H=5830

5461

(p)

Fig. 8.

(s)

H=16400

61

(s)

Fig.

H=15

Echelon  
L.G. Plate

800

5461

Fig. 9a.  
(enlarged.)

H=17800 (p) only.

Fig. 11.

Fig.

(p)

(s)

5461

Heterogeneous Field.

H: 15800 to 30000





5461

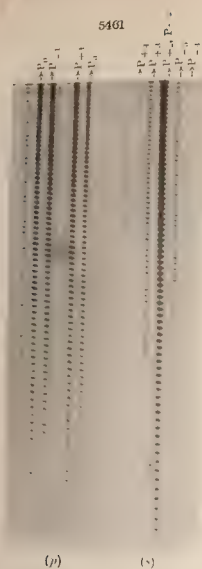


Fig. 1.

 $H = 1700$ Echelon and  
L.G. Plate.

5461



Fig. 2.

 $H = 17300$ Echelon and  
F.V. Plate.

5461

(p)

Fig. 6.

(s)

 $H = 17400$ 

5461

(p)

Fig. 7.

 $H = 18500$ 

(p)

Fig. 8.

(s)

5461

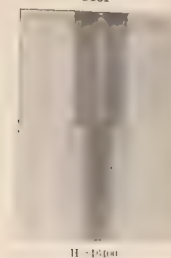
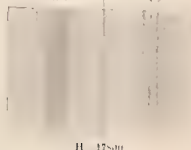
 $H = 18600$ 

Fig. 9.

(p)

5461

(s)

 $H = 17800$ 

5461

Fig. 9a.

(enlarged.)

 $H = 17800$  only

Fig. 4.

4047  
Heterogeneous Field.  
 $H = 5300$  to  $11500$ .

Fig. 5.

4047  
Heterogeneous Field.  
 $H = 12700$  to  $32000$ .

Fig. 3.

(p)

(s)

4047

 $H = 7150$ 

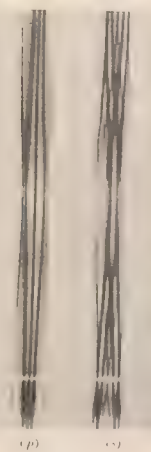
Fig. 10.



5461

Heterogeneous Field.  
 $H = 9200$  to  $18900$ .

Fig. 11.



5461

Heterogeneous Field.  
 $H = 15000$  to  $30900$ .



THE  
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AND  
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

MARCH 1914.

XLIV. *Interference Experiments in a Highly Rarefied Gas.*  
By F. P. KERSCHBAUM, Ph.D. (Leipzig), B.A. (Caius  
College, Cambridge)\*.

[Plate VI.]

*Introduction.*

THE assumption of a discontinuity of some kind in the processes of the elementary radiation seems to be inevitable. This Planck† has shown in his successful attempt to explain temperature radiation. Quite generally such an assumption follows from the fact that very probably Hamilton's equations, according to which physical processes can be represented by differential equations, *i. e.* continuously, do not hold in certain cases. The doubt about the general validity of Hamilton's equations is justified by the fact that a consequence of these equations, the law of equipartition of energy, is not in accordance with experimental results‡. Moreover, Jeans§ was able to show that Hamilton's equations, combined with the theory of probability, lead to Rayleigh's radiation formula, which is contradicted by experiments. The introduction of discontinuous radiation processes is, in fact, accomplished both in the radiation hypothesis of Planck

\* Communicated by Prof. Sir J. J. Thomson, O.M., F.R.S.

† M. Planck, *Ann. d. Phys.* iv. p. 553 (1901), and *Theorie der Wärmestrahlung*, Leipzig, 1912.

‡ Comp. the recent work of Nernst and his pupils on atomic heat, e. g. *Z. f. Elek. Chem.* xvii. p. 272 (1911).

§ Jeans, *Phil. Mag.* xviii. p. 209 (1909).



and in that of J. J. Thomson by the conception of "quanta" or "units" respectively.

*The Radiation Hypotheses.*

According to the latest form of Planck's hypothesis, only the elementary energy transformation is a discontinuous process. Emission of light—and this emission only—is a quantum process, because the elementary oscillator is only able to radiate energy in amounts  $\epsilon = h\nu$  or whole multiples of it. The emitted energy spreads in continuous waves, as on Maxwell's theory, and is absorbed continuously. Planck's hypothesis, therefore, only introduces a discontinuity in time. His view is very successful in its applications to thermodynamical problems. For the purely optical phenomena it does not bring anything new.

J. J. Thomson\*, however, assumes a discontinuity in the energy. Radiation energy itself has structure. Not only does the elementary oscillator radiate energy in certain amounts, but this energy is also concentrated in certain parts of space. Radiation energy is built up from "units." J. J. Thomson arrived at his views by imagining that electromagnetic disturbances can only be propagated along the lines of force. So the light unit represents a disturbance in the lines of force over a cross-section of corpuscular dimensions, but of considerable length, carrying a whole train of periodic oscillations. Such units can explain the phenomena of gas ionization by ultra-violet light, the photoelectric effect, and the inter-convertibility of cathode and X-ray energy.

Einstein† too arrived at the conception of independent light-cells from the consideration that monochromatic radiation of not too high intensity may be treated thermodynamically like a gas. From this point of view and in accordance with Planck, his light cells are not capable of subdivision. They carry the energy amount  $\epsilon = h\nu$ , where  $h$  is Planck's constant.

In spite of this evident success of energy units for the explanation of the different ionization phenomena, the assumption of a structure of the energy has not been

\* J. J. Thomson, 'Electricity and Matter,' 1903. In this connexion it is perhaps interesting to notice that it is not possible to attribute to a light unit all the same properties as to an equally small volume in a parallel beam of light-waves. As the cross-section of a unit—in order that such a unit may be of any use at all—has to be very much smaller than any wave-length, Huyghens' principle cannot be applied to a beam of this small cross-section. In fact, from Huyghens' principle, it would follow that such a light unit, if coming into existence at all, must disappear at once, the energy being radiated uniformly in space.

† Einstein, *Ann. d. Phys.* xvii. p. 132 (1905).

generally accepted, as the opinion is held that the hypothesis of a unit emission is in contradiction with the laws of optics and cannot explain diffraction and interference experiments.

*Attempt to explain from the unit point of view the  
Interference experiments hitherto known.*

J. J. Thomson has, however, shown\* that all the interference experiments known till now, can be explained by the supposition of corpuscular units—at least qualitatively,—if one assumes that the energy in the light unit remains only invariable as long as this unit does not pass through matter. In passing through matter, it sets up resonance vibrations among the systems of electrons. These vibrators, therefore, take up energy from the primary unit and become themselves centres for the emission of secondary units. All these secondary units are, among each other and with the primary unit, in fixed phase relation due to resonance. This increase in the number of centres for unit emission together with the phase relation will produce in interference experiments much the same effect as light-waves.

“If light, however, were produced in a gas at a very low pressure we should expect that in the gas itself the energy in the radiation emitted by a luminous atom or molecule would not be nearly so much subdivided as after it has passed through the glass walls of the tube enclosing the gas, and so that the energy in the light inside the vacuum-tube might be not nearly so uniformly distributed through space as when it got out of the tube. It would be interesting to test this point by seeing whether interference-fringes could be produced as easily and to the same extent in a good vacuum as under ordinary conditions, the light being produced in the vacuum either by the electric discharge or preferably by canal-rays.”

If it is, therefore, possible to make a gas emit light at such a low pressure that an emitted light unit of corpuscular cross-section on its way through the gas has practically no chance of hitting a molecule of this gas, no resonance can come into play. And interference experiments under such conditions will lead to definite conclusions with regard to the resonance hypothesis.

The whole resonance hypothesis rests, of course, on the supposition that a single light unit alone or a random succession of units is not able to produce something like interference-fringes, when passing over an interference apparatus.

\* J. J. Thomson, Camb. Phil. Soc. Proc. xvi. p. 643 (1912).

In fact, with the conception of the unit alone as sketched above,—*i. e.* as a train of oscillations moving along the tube of force in something like a straight line,—we cannot account for interference.

So we have only to make sure for our experiments that the source of light which we are going to use does not emit the units with any regularity, so that the different units do not arrive at the interference apparatus with a fixed phase relation. We shall show later that this is the case in our arrangement.

### *The Source of Light.*

The condition that light units of corpuscular cross-section can escape from a gas which has to act as source of light and at the same time necessarily fills the whole of the interference arrangement without practically being stopped by the molecules of the gas, is fulfilled, if the total cross-section of the gas molecules, contained in a column of the length of the apparatus, is small compared with the cross-section of this column. We shall see later that the length of a suitable interference apparatus is about 50 cm. From the known numbers and dimensions of the gas molecules we can therefore conclude that *e. g.* for  $H_2$  the pressure of the gas in the apparatus would have to be about 0.0001 mm., if only 0.1 of a given cross-section is filled with  $H_2$  molecules; in other words, at a pressure of 0.0001 mm. only 10 per cent. of the emitted light units are liable to hit  $H_2$ -molecules. The order of magnitude of this pressure is about the same for all the gases.

Now it is known that canal-rays in a gas of or under 0.01 mm. pressure already emit light which is too feeble for interference experiments of finite duration. The direct production of light in gases at such low pressures, as required above, seems therefore not to be practicable by any sort of electric discharge. Moreover, such light is never homogeneous, and therefore not suitable for interference experiments in which the result depends upon the distinctness of the fringes.

In his recent work on the fluorescence of vapours Wood\* has discovered a very interesting source of ultra-violet light. Hg-vapour in a vacuum at room temperature, *i. e.* at a partial pressure of about 0.001 mm., can be excited to fluorescence radiation by illumination with light-waves of the wave-length  $\lambda = 2536 \text{ \AA.U.}$  This fluorescence light is entirely monochromatic and of the same wave-length as the exciting light, it is scattered resonance light. It corresponds to the sharp

\* R. W. Wood, Phil. Mag. xxiii. p. 689 (1912).



absorption line of the Hg-vapour at  $\lambda=2536$ . According to Wood (*l. c.*) its intensity is reduced to the half value by passing through a 5 mm. thick layer of Hg-vapour of 0.001 mm. pressure. It shows no trace of polarization.

There is hardly much doubt that the exciting light increases the amplitude of a prominent frequency in the Hg-atom till it emits light, without, however, ionizing the vapour. About the mechanism of this process nothing is known at all. We do not even know what the ratio is of the number of radiating molecules to the total number of molecules for a given intensity of the exciting source.

Considering the limit of pressure, mentioned above, it seems at first sight that even Hg-vapour at 0.001 mm. pressure is still about ten times too dense in order that its resonance radiation may be used for the proposed experiment. Fortunately that is not the case. For Hg-vapour, being a vapour, does not necessarily fill a whole vacuum with uniform density. An experiment, described later, will show that saturated Hg-vapour can fill uniformly one chamber, while in a second chamber, in connexion with the first one by means of a narrow slit, the Hg-vapour pressure can be kept practically at zero, if in this chamber the Hg-vapour is condensed much more rapidly than it is supplied by diffusion through the slit. For our experiment the first chamber, filled with Hg-vapour in resonance radiation, is to be used as source of light; the second chamber has to contain the interference arrangement. The condition that this second chamber must be practically free from Hg-vapour in our case has to be fulfilled for another reason still: the resonance radiation coming from the first chamber would be absorbed entirely before reaching the interference arrangement.

If it is possible to excite Hg-vapour of 0.001 mm. pressure in a layer of only 1 or 2 cm. thickness to a sufficiently brilliant light emission, the resonance radiation of Hg-vapour seems to be a source of light for our experiments.

But before we arrive at this conclusion we have to discuss the point, already alluded to: As the Hg-vapour is radiating only under the influence of an exciting source of light, which we assume supplies the energy in waves, the question arises whether these waves perhaps enforce upon the radiating systems of the Hg-vapour some sort of fixed phase relation between the emitted units.

But this could happen only

(1) if we would have to assume that the trains of oscillation only come from radiating Hg-molecules in optical



distances  $d + an$  from the interference apparatus (where  $d$  is the distance between the interference apparatus and one of the resonating systems,  $n$  an integer, and  $a$  an arbitrary constant). Only then could the trains arrive at the interference apparatus with a constant difference in phase, or in the same phase if  $a=2$ . But any such arrangement of molecules is incompatible with the conception of a random distribution of the molecules in a gas, independent of any proper motion of these molecules ;

(2) or if the Hg-molecules with their random distribution in space take up the energy of the incident waves at an individual and very special rate, so that the radiating systems begin to discharge the trains of oscillation in a most complicated and peculiar succession of moments only.

Then again we could imagine that the different units arrive at the interference apparatus with a constant lack in phase. But we have every reason to assume that this special process is beyond the limit of any probability.

So we can be sure that resonating Hg-vapour will behave just like an independent source of light.

### *The Optical Arrangement.*

The method of producing interference-fringes for our purposes must fulfil the condition that the light does not hit matter before it has passed the interference system. This condition is fulfilled in Young's arrangement: Light from a line source passes through a double slit and afterwards falls upon a screen. In the case of wave radiation we get—as is known sufficiently well—on the screen a system of fringes. The pattern can be explained by the conception that the double slit acts as two independent sources of radiation. Each slit produces its own diffraction pattern on the screen. Both diffraction patterns overlap and, in doing so, give rise to the production of interference-fringes, because the light passing through the double slit is in a fixed phase relation. The spectra of different order, as produced by the diffraction, are crossed with lines of greatest intensity separated by lines of smallest intensity in places where the path difference of the rays from the two slits is  $m\lambda$  and  $\frac{2m+1}{2}\lambda$  respectively ( $m$  being an integer).

If, however, light units with no definite phase relation between them pass through the double slit, the formation of a diffraction or interference pattern cannot take place. On the screen we would have only to expect two lines of light in places where the straight lines drawn from the source of

the light through the double slit hit the screen, just as if X-rays were emitted from the line source.

But Young's simple arrangement is not powerful enough for our purpose. For in order to produce with it distinct interference-fringes, even with monochromatic light, the distance between the source of the light-waves and the screen—or the photographic plate in the case of ultra-violet light—must be several metres. It requires brilliant light or very considerable exposures. Now to maintain a vacuum of at least 0.00001 mm. pressure in such big vessels for a couple of days or even weeks is certainly rather difficult and hopeless if the vacuum apparatus has to be built to hold a photographic plate.

But Fraunhofer's modification of Young's arrangement helps over this difficulty. The double slit is placed right in front of the objective lens of a telescope or a telephoto camera. I find that by this arrangement the distance between the line source of light and the double slit can be reduced to about 60 cm. when a telephoto camera of only 28 cm. length is employed. The telephoto camera enlarges only the interference pattern. The camera of the construction to be described later, produces the narrow interference-fringes which cross the diffraction pattern of the order nought in great intensity. The fringes in the spectra of higher order are, however, much weaker; they only appear at the plate when the central fringes are already much overexposed. The distinctness of the interference-fringes does not suffer if the openings in the double slit are made rather wide, between 0.04 and 0.08 mm., and in doing this the gain in intensity is very great. But the first slit representing the line of light must not be wider than 0.02 mm.

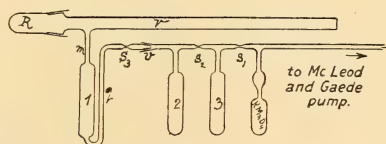
It is evident that for a wave radiation the introduction of a telephoto arrangement does not alter the character of the phenomenon under consideration.

But for light unit radiation, according to the views given above, a change of theoretical importance will occur. The light units after passing through the double slit fall upon the front of the objective lens, *i. e.* on matter, and can excite there resonance emission along two lines forming sources of something like a continuously spreading wave. As this sort of wave only comes into existence at the lens, *i. e.* behind the double slit, and as its course is not limited by any obstacle, no diffraction or interference pattern can be obtained on the photographic plate of the telephoto camera. We have, therefore, to expect a patch of uniform illumination on the plate with its centre at the spot where for wave radiation the interference-fringes are most distinct.



short brass cylinder fits tightly. The end of this cylinder is closed by a brass disk bearing the slit ( $s$ ), which has to act as the line source of light. This slit was made in the following way: two plane brass plates of 15 mm. length,

Fig. 3.



12 mm. height, and 1 mm. thickness, were pressed together with a strip of copper-foil between them, of 0.02 mm. thickness. The brass plates were soldered together by means of a small brass band along the top and bottom edge; afterwards the copper-foil was pulled out. In this way a slit was got of 0.02 mm. width, 12 mm. height, and 15 mm. length.

The other end of the quartz-glass tube ( $t$ ) has a short ground surface on the inside. Into this surface fits a thin conical ring ( $d$ ) of nickel-steel, 5 mm. long. Across the ring a thin sheet of copper is soldered in which two parallel openings are cut with a knife, forming the double slit. Each of these cuts is about 12 mm. long, 0.05 mm. wide; they are 1 mm. apart. Now the ring with this double slit is pressed tightly into the corresponding ground face at the end of the quartz tube. After this the brass tube carrying the slit ( $s$ ) is put on the front end and turned round till both slit systems are parallel to each other. If the slit ( $s$ ) is in a symmetrical position to the double slit at the other end of the quartz tube, interference-fringes can be seen when looking through the system, the slit ( $s$ ) being held towards a source of light and the double slit in front of the eye. Great care has to be taken to find the symmetrical position of the slit systems giving the greatest possible intensity and distinctness of the fringes. The friction in the ground surfaces keeps front and double slit in a fixed position relative to each other. The whole tube ( $t$ ) with its optical arrangement is then pushed into a quartz-glass tube ( $n$ ) of 20 mm. interior diameter till the ground surface ( $q$ ) on the inside quartz tube ( $t$ ) fits into the corresponding ground surface ( $g$ ) of the outside tube ( $n$ ). The other end of this tube is closed with a plane-parallel plate of transparent quartz-glass fused on the tube. The outside tube is just so long that the inside tube with the double slit reaches right up to the plane-parallel plate if the tube makes a tight fit in the



ground joint ( $g$ ), the distances between the double slit and the quartz plate being 1.5 mm. The ground joint ( $g$ ) holds the long tubes in a fixed position and at the same time prevents a rapid diffusion of the Hg-vapour from the chamber (R) in front of the slit ( $s$ ) into the part behind this slit, the chamber (V).

The quartz-glass tube ( $n$ ) has still another ground surface ( $f$ ) at the very front end. On this fits a sort of cap of transparent quartz-glass with the corresponding ground surface ( $f'$ ). The interior of this cap forms the chamber (R) just mentioned above, in which the resonance radiation of the Hg-vapour has to be produced. The Hg-vapour is supplied from a drop of mercury which is introduced in a small side-tube ( $o$ ) before the apparatus is put together. For the incidence of the radiation of the existing Hg arc-lamp a special window ( $w$ ) is provided in the cap. It is a short quartz-glass cylinder of 5 mm. length and of 15 mm. diameter with flat bottom, quite free from air-bubbles. This window forms a depression in the cap, as shown in figs. 1 and 2. By this arrangement we get intense illumination just in front of the slit ( $s$ ). Window ( $w$ ) and slit ( $s$ ) have such a position relative to each other that a beam of parallel light passing normally through the window does not hit the front of the slit but passes about 2 mm. away from it. At the outside the cap is carefully blackened, with the exception of the flat window ( $w$ ) of course.

By reflexion from the walls of the chamber (R) some light from the exciting arc-lamp can come through the slit ( $s$ ). But experiments will show that the intensity of this stray light is only a few per cent. of the intensity of the resonance radiation. The resonance (and stray) light filling the chamber (R) is stopped from entering the chamber (V) by any path other than the slit ( $s$ ) by coating the quartz tube ( $t$ ) with liquid platinum burned into the surface.

When ready for an experiment the ground surfaces ( $f$ ) of the cap and tube ( $n$ ) are warmed with a blowpipe, some sealing-wax\* put on the warm joint and the cap gently pressed on the tube. In this way a perfect seal can be obtained. For the critical experiment, however, this seal is not perfectly free from objection, and in this case another method of sealing was used. The ground surfaces ( $f$ ) are put together, the apparatus turned vertically and the rim filled with mercury. Joint and mercury are warmed up with the blowpipe and when hot covered with a layer of

\* The white quality with low vapour-pressure and low softening-point being employed.

sealing-wax. After cooling down, the apparatus can be placed horizontally, the Hg being kept in position by the solid layer of sealing-wax. In this way an intrusion of vapours due to the sealing-wax is entirely prevented. The diffusion of the Hg-vapour between the ground surfaces ( $f$ ) does not matter, because the joint ( $f$ ) leads to the chamber (R) already saturated with Hg-vapour from the drop ( $o$ ).

For the exhaustion of the whole vessel, the quartz tube ( $n$ ) has a wide side tube ( $m$ ) which leads to a wide quartz tube (1 in fig. 3). This tube is filled with charcoal and when submerged in liquid air is supposed to condense the Hg-vapour, coming through the slit ( $s$ ). In order to procure ample connexion between the chamber (V) and this charcoal tube, a hole ( $h$ ) is blown into the quartz tube ( $t$ ) (compare fig. 1) just opposite the side tube ( $m$ ). This side tube ( $m$ ) is fused on the tube ( $n$ ) as near as possible to the ground joint ( $g$ ).

The quartz tube ( $q$ ) connects the quartz charcoal vessel with the rest of the apparatus provided for the exhaustion, which is made of ordinary glass. Quartz tube and ordinary glass tube are cemented together with sealing-wax at ( $r$ ). As shown in the figure, two more charcoal tubes are provided and a tube containing some  $\text{KMnO}_4$ , for washing with  $\text{O}_2$ , a Gaede pump and a MacLeod gauge (300 c.cm.).

At ( $s_1$ ), ( $s_2$ ), ( $s_3$ ) places are provided where the glass, resp. quartz tubes can be sealed off. No taps are provided at all.

During an interference experiment the evacuated quartz apparatus is held horizontally by two solid supports of a big optical bench, which is free from vibrations. On the same optical bench the telephoto camera slides, carried by two solid supports. This telephoto camera (comp. fig. 1) consists of a wide brass tube which holds the objective lens  $l_1$  of 10 cm. focal length and 5 cm. diameter. At a distance of 130 mm. the lens  $l_2$  is placed, of 2 cm. focal length and 2 cm. diameter. The end of the brass tube carries a support for a photographic plate-holder. The distance between the lens  $l_2$  and the plate ( $a$ ) is 150 mm.

The telephoto camera is brought right up to the plane-parallel quartz plate ( $p$ ) of the vacuum vessel. It was found empirically that such a camera in connexion with the double-slit arrangement, as described above, could produce interference-fringes of suitable dimensions, quite distinct and numerous enough.

The light of the wave-length  $\lambda = 2536 \text{ \AA.E.}$ , exciting the Hg-resonance radiation, was supplied from an Hg arc-lamp of special construction. The arc of this lamp emits light

containing the frequency which is capable of exciting the Hg-resonance radiation in very high intensity and continuously\*.

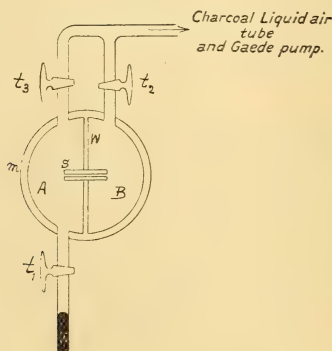
*On the Velocity of the Diffusion of Hg-vapour at room temperature.*

The apparatus, described above, will only work satisfactorily if it is possible to maintain the partial pressure of the Hg in the chamber (V) under 0.00001 mm., while in the chamber (R) this pressure is 0.001 mm., the partial pressure of air in both chambers being under 0.00001 mm. The Hg-vapour which diffuses through the slit (*s*) is to be condensed by liquid air. Is this diffusion slow enough compared with the velocity of the condensation for the dimensions of our apparatus?

This question was decided by the following experiment, in which we use the extraordinary facility with which resonance radiation is scattered, *i. e.* apparently absorbed by saturated Hg-vapour at room temperature.

A brass cylinder (*m*) (fig. 4) of 3 cm. length and 3 cm.

Fig. 4.



diameter is closed at both ends with quartz crystal plates cemented on with sealing-wax. Along the axis the cylinder is divided into two halves (A) and (B) by means of a brass plate (W). Into this partition wall a slit (*s*) is soldered of the same dimensions as used in the interference apparatus. The halves (A) and (B) are therefore only connected by a slit of 0.02 mm. width, 12 mm. height, and 15 mm. length. The slit (*s*) is shown horizontally in fig. 4. Two brass tubes

\* I intend to publish shortly a detailed account of the construction of this lamp and the properties of its light.

lead into (A), one into (B). Over these brass tubes, glass tubes with glass taps are cemented with sealing-wax. They are connected as shown in the figure. Through the tap ( $t$ ) a drop of Hg can be brought into (A). By means of the taps ( $t_2$ ) and ( $t_3$ ) the halves (A) and (B) can be separated from the rest of the apparatus, *i. e.* a charcoal-liquid air-tube and a Gaede pump.

This absorption cell is placed in front of a resonance lamp (comp. Wood, *l. c.*), *i. e.* in our experiment a bulb made of transparent quartz-glass of 3 cm. diameter, filled with pure Hg-vapour of 0.001 mm. pressure. This Hg-vapour is excited to resonance radiation by means of sideways illumination with the special Hg arc-lamp. Then the whole quartz-bulb emits light rather uniformly and of great intensity in the line 2536 Å.E. and with very little stray light. The distance between resonance lamp and absorption cell is 10 cm. The resonance light passes through the absorption cell and then falls upon a uranium-glass plate held in front of the cell, exciting strong fluorescence in the uranium glass.

To carry out the experiment, we proceed in the following way:—The whole apparatus, as shown in fig. 4, is pumped out with a Gaede pump, while all taps are open till the air-pressure of about 0.00002 mm. is reached. After this, the tap ( $t_1$ ) is closed. Now the charcoal tube is submerged in liquid air and all traces of Hg-vapour from the halves (A) and (B) are completely absorbed. Then taps ( $t_2$ ) and ( $t_3$ ) are closed. At this stage the light of the resonance lamp passing through the absorption cell produces two bright fluorescence patches on the uranium glass of equal intensity. Now tap ( $t_1$ ) is opened and a drop of mercury is allowed to enter (A). Immediately the light patch, due to the radiation through the half (A), disappears entirely and only a few seconds later the light patch due to (B) disappears too. But by opening now tap ( $t_2$ ), and therefore connecting the half (B) with the charcoal-liquid air vessel, (B) immediately brightens up and in a few seconds is as bright as at the beginning of the experiment. But (A) remains dark.

From this experiment we can deduce the following conclusions:—

(i.) That a drop of Hg at room temperature is able to fill a chamber immediately (practically) and is able to keep it filled with saturated vapour, even if from this chamber the Hg-vapour is sucked away through a slit of the given dimensions by liquid air.

(ii.) That a slit of the dimensions mentioned above allows of remarkably rapid diffusion.



(iii.) That in spite of this rapid diffusion the velocity of this diffusion is very small compared with the velocity of the condensation of the vapour by liquid air through tubes of a cross-section large compared with the cross-section of the slit.

### *The Experiments.*

With the interference apparatus as described above the following experiments were carried out :—

(I.) The quartz vessel, shown in figs. 1 and 3, was evacuated by means of working the Gaede pump only, till a partial pressure of the remaining air was about 0.002 mm. After this the special Hg arc-lamp which has to excite the Hg-vapour to resonance radiation in chamber (R) was brought up to the apparatus opposite the window (*w*) as close as possible. A parallel beam of light enters the vacuum without, however, raising the temperature of the chamber appreciably, because the light of the arc-lamp has first to pass a layer of water which is cooling the lamp. An exposure of the photographic plate\* is then made of two hours' duration. After developing, no trace of any light action can be detected on the plate. Only an exposure of about ten hours' duration produces a few very faint fringes. But these fringes are not sharp, and they are distant from each other about twice as much as they should be for light  $\lambda = 2536$ . In fact, these fringes are only due to the stray light entering through the slit (*s*). Indeed, fringes due to the resonance radiation of the Hg-vapour in the chamber (R) cannot be expected in this experiment, as the whole chamber (V) is filled with saturated Hg-vapour. The resonance light, coming through the slit, is totally absorbed in passing through this chamber.

(II.) The experiment is repeated at the same partial pressure of air, but before starting the exposure the quartz condensation-vessel (1, fig. 3) is submerged in liquid air and kept there during the exposure. Ninety minutes' exposure now give about twenty fringes, as shown in fig. 1 (Pl. VI.). They are sharp fringes showing the proper distance which is to be expected for light of  $\lambda = 2536$ . Owing to the short exposure no traces of fringes due to the stray light can be detected.

From the relative times of exposures in these experiments we can roughly deduce that the intensity of the resonance

\* Lumière plates "Violet Label" were used throughout.

light is about twenty times the intensity of the stray light, measured by their photographic activity. This despite the fact that the resonance light is weakened by absorption in passing through the slit (*s*) which contains Hg vapour necessarily.

(III.) In order to get some idea of this amount of Hg-vapour in the slit and the chamber (V) during the experiment just described, I proceeded as follows:—

The cap (R, fig. 1) was removed and the apparatus thoroughly washed with CO<sub>2</sub> from a cylinder. Now a resonance lamp as used in the diffusion experiment\* is brought right up in front of the slit (*s*), which in this experiment is free from traces of Hg-vapour, as well as chamber (V). Then the resonance lamp is excited. An exposure of eighteen minutes gives fringes as shown in fig. 2 (Pl. VI.). They are practically as intense as the fringes shown in fig. 1. Bearing in mind that a layer of about 5 mm. thickness of saturated Hg-vapour reduces the intensity of the resonance light to the half value, the ratio 5 : 1 for the times of exposure in experiments (II.) and (III.) indicates that the light in experiment (II.) has to pass a vapour layer of about 12 mm. thickness if saturated. Now the slit (*s*) is itself 15 mm. long. We have therefore to imagine that, when the charcoal is condensing the Hg-vapour, very probably only the slit (*s*) is filled with this vapour, and that in the chamber (V) the partial pressure is under 0.00001 mm. For a column of 500 mm. length of Hg-vapour of this pressure would correspond to a layer of 5 mm. thickness of saturated Hg-vapour, and would therefore cause absorption, which could be detected.

Anyhow, from experiments (II.) and (III.) we can draw the conclusion, that the light emitted from the resonance chamber (R) in experiment (II.) has, after leaving this chamber, only to traverse a layer of Hg-vapour equal to a layer of 12 mm. thickness of saturated vapour, before reaching the double slit.

A light cell emitted in the resonance chamber (R), where the centre of the bundle of the exciting rays passes—*i. e.* in about 9 mm. distance from the slit (*s*)—has therefore to pass a Hg-vapour layer of about 21 mm. thickness and of 0.001 mm. partial pressure. If the partial pressure of the air is small enough to be neglected for our purposes, this means that not more than 16 per cent. of such emitted light cells can possibly hit Hg-molecules, *i. e.* matter, before they

\* Giving resonance light of the same intensity as the chamber (R) if excited with the same special Hg arc-lamp.

reach the double slit. The other 84 per cent. pass through the resonance chamber (R) and chamber (V) without being stopped.

This layer of saturated Hg-vapour of 21 mm. thickness represents the limit to which I could proceed in reducing the density of the matter acting as source of light and filling the interference apparatus at the same time. One might imagine that these conditions could be improved very much by using the resonance radiation of Hg at a lower temperature still, *i. e.* by keeping the drop which supplies the vapour at a lower temperature. This, however, is hardly possible. While the intensity of the resonance radiation would be greatly reduced in this way, at the same time the intensity of the exciting light and therefore the amount of stray light would have to be unaltered. But if resonance light and stray light have intensities of the same order of magnitude, the experiments will not prove anything.

(IV.) The critical experiment is performed now in the following way:—

The same arrangement is used as in experiment (II.) and described fully p. 410, but every care is taken to reduce the partial pressure of the air so much, that the traces of gas still left in the apparatus are absolutely to be neglected.

The apparatus (comp. fig. 1) is evacuated with the Gaede pump till the McLeod shows a pressure of about 0.00002 mm. During the working of the pump the whole quartz apparatus (with exception of the cap carrying the drop of Hg and the mercury-sealing-wax seal) is heated up with the blowpipe and the glass charcoal vessel warmed as high as possible and kept warm. Now the  $\text{KMnO}_4$  vessel is gently heated till  $\text{O}_2$  fills the apparatus to a few mm. pressure. The  $\text{O}_2$  is pumped off, and this washing with  $\text{O}_2$  repeated again. After this washing, while all the absorption vessels are hot still, the McLeod is showing a pressure of 0.00001 mm. and the Gaede pump is working, the quartz apparatus with the two glass charcoal vessels is sealed off at  $s$  (fig. 3) from the rest of the apparatus, *i. e.* the  $\text{O}_2$ -developer, the McLeod and the Gaede pump. Then the absorption-tube (3) is allowed to cool down and is submerged in liquid air. After two hours this absorption-tube is sealed off at  $s_2$ . The absorption-tube (2) is now allowed to cool down and then submerged in liquid air. In this state the apparatus is kept for four hours. Then the quartz tube ( $q$ ) is sealed off at  $s_3$  with a coal-gas-oxygen blowpipe. The production of the vacuum in this way takes two days. As the apparatus was sealed off from



the Gaede pump when the gas pressure was already 0.00001 mm., as indicated by the McLeod gauge, I feel sure that the partial pressure of gas finally was under 0.000001 mm.

Now the quartz apparatus is ready for the experiment. It is brought on the optical bench, put in position, and the condensation-chamber (1) submerged in liquid air. Then an exposure is made. Thirty minutes give a photo as shown in fig. 3 (Pl. VI.), ninety minutes in fig. 4: in both cases very distinct fringes. In fact, fig. 4 (Pl. VI.) shows the fringes of practically the same intensity as fig. 1 (Pl. VI.).

No trace can be found of any diminution in number or distinctness or intensity in fringes if produced in a gas of very low pressure, compared with the appearance of fringes, given by the same apparatus at atmospheric pressure.

### *Conclusions.*

The experiments show that we have no reason to assume that a subdivision of light units is taking place when these units pass through matter. The resonance hypothesis is therefore not able to reconcile the existence of interference phenomena with the conception of "units" sketched above.

But are we forced by this experimental result to assume the hypothesis that the energy of the elementary radiator is only spreading in spherical waves? Not, if we succeed in developing a conception of a unit which produces effects similar to those of waves when falling upon an interference arrangement.

Such a conception seems, in fact, possible.

According to J. J. Thomson we should not assume that a line of force is more or less at rest and could not have rapid sideways motion. Then, of course, a succession of oscillations travelling along such a moving line is no longer propagated in a straight line. Therefore, we can imagine quite well that different parts of one and the same train of oscillations are passing through both slits of the interference arrangement used in our experiments. If all the lines of force move across the interference apparatus at the same rate, the parts of the trains which pass through the slits will have a constant lack in phase. So we should get a pattern much the same as we should expect for waves.

With regard to the velocity of the sideways motion of a line of force, we are practically not limited as this velocity represents a change in direction and not a real velocity.



So we can go one step further.

We assume an atom model with electrons rotating round a central body, lines of force originating from the electrons and disturbances travelling along them. A line of force originating normally to the plane of rotation of the electron will not have much motion, and a train of oscillations (even of considerable length) travelling along this line will be in something like a straight line. But on a line of force in the plane of the rotation of the electron, a train of oscillations will not be emitted as a whole in a certain direction; if the motion of the electron is only rapid enough the train of oscillations (representing a succession of up to many hundred thousand periods) will be emitted in a spiral with a very considerable number of turnings. These spirals spread. As a finite source of light will emit them in random directions, these spirals will produce effects similar to those of spherical waves when falling upon an interference apparatus.

From the fact that very distinct interference-fringes can be got experimentally, we would have to deduce that the energy emitted from a source of light in straight trains is very small compared with the energy emitted in such spirals.

These views form perhaps the foundation for a combined explanation of the purely optical phenomena and of the ionization effects.

Such a conception of the energy emission of the elementary oscillator would avoid a dualism to which Marx \* alludes in the explanation of his photoelectric experiments. He thinks of waves with points of concentration, and finds that the amount of energy localised in these points need not be more than a small fraction of the energy contained in the wave.

#### *Summary.*

- (i.) Interference experiments are described where the source of light and the interference apparatus are in the same highly evacuated vessel.
- (ii.) The source of light employed is the resonance radiation of Hg-vapour excited to continuous luminosity by a special Hg-vapour lamp.
- (iii.) The experiments show that a "resonance" hypothesis developed for an explanation of the purely optical phenomena by units does not represent the facts.

\* E. Marx, *Ann. d. Phys.* xli. p. 167 (1913).

- (iv.) The conception of the "unit" is extended. In this form, units promise to become successful in the explanation of the purely optical effects.

In conclusion I wish to express my best thanks to Sir J. J. Thomson for his kind interest in these experiments.

Cavendish Laboratory, Cambridge.  
August 1913.

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XLV. *Cathode Disintegration in a Vacuum Tube.* By A. M. TYNDALL, *D.Sc.* (*Lecturer in Physics in the University of Bristol*), and H. G. HUGHES, *B.Sc.*\*

THE disintegration or "spluttering" of the cathode in a vacuum tube has been the subject of much investigation. A comprehensive summary and discussion of the results which have been obtained has been published by Kohlschutter †, and to his paper a complete bibliography is appended.

In the following paper an account is given of some further experiments on the influence of certain factors on disintegration. The effects of some of these factors have already been a subject of investigation, as may be seen by reference to the literature of the subject, but it was felt that there were a number of points upon which further information was necessary.

The factors dealt with below are (a) the duration of the discharge; (b) the previous history of the cathode; (c) the pressure and nature of the gas; (d) the current density; and (e) the cathode fall of potential. A summary of the conclusions which have been arrived at is given at the end of the paper.

#### *Method of Experiment.*

The amount of disintegration was measured in all cases by the loss of weight of the cathode. During discharge it was necessary in general to control and measure pressure, current, and cathode-fall of potential. A diagram of the experimental arrangements is shown in the figure.

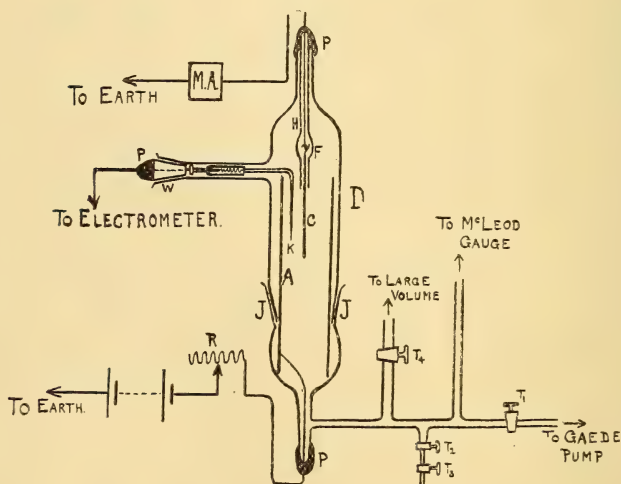
D is the discharge-tube which could be opened at the

\* Communicated by the Authors.

† Kohlschutter, *Jahrbuch d. Rad. u. Elektronik*, ix. p. 355 (1912).

ground-glass joint J. The cathode C was hung by a hook F from wire enclosed in a glass sheath H, and the cathode-fall of potential was measured by an exploring wire K consisting of fine platinum wire protruding 1 mm. from the end of a glass sheath. The potential difference between K and C was measured by a Braun electrometer. The distance between K and C could be varied by turning the ground-glass joint W to which was attached a suitable screw arrangement.

Fig. 1.



The anode was in most cases a brass cylinder A, and was connected to the high potential pole of a battery of small accumulators. In some cases, however, a small aluminium plate was used as anode, in which case the brass cylinder A was replaced by one of glass, to collect most of the deposit and to prevent cathode rays from striking the grease of the ground joint. It was found, however, that under these conditions the deposit collected very readily on the glass sheath of the cathode, forming a film of metal which in time joined with the cathode in discharging; it was then necessary of course to stop the discharge. It is probable that this deposit on the sheath was due to a repulsion between the negatively-charged particles of disintegration and the charge acquired by the glass surroundings. The cylindrical form of anode greatly diminished this effect and had the additional advantage of ensuring a symmetrical form of discharge. The cathode was earthed through a milliammeter (M.A.), and the

current through the tube was adjusted by a sliding liquid resistance (R) of amyl alcohol and cadmium iodide.

Glass taps  $T_1$  and  $T_4$  connected the vessel D to a Gaede pump and a 10-litre bottle respectively. The taps  $T_2$  and  $T_3$  were joined by 8 cm. of capillary tubing: by these gas could be admitted in small quantities into the apparatus. The joints were either of blown glass or made airtight with picein. The pressure was measured by a McLeod gauge. Any deposit on the tube, cathode sheath, and exploring wire was removed before each fresh discharge.

In general, the cathodes were platinum wires, but in some of the earlier work copper wires were used. These were 4 mm. in diameter and 5.75 cm. long. The platinum cathodes were for the most part 1.35 mm. in diameter and of exposed length 6 cm. The ends of the cathodes were hemispherical. The cathodes were weighed before and after discharge on a balance weighing to 0.1 mg., it being arranged that differences in weight were measured in every case in terms of the rider.

### RESULTS.

The statement of results falls naturally into certain sections.

#### *Early Stages of Discharge.*

Experiments were carried out first with copper and later with platinum cathodes on the following points:—

- (a) The effect of leaving the cathode *in vacuo* previous to use.
- (b) The effect of previous discharge from a cathode on its subsequent rate of disintegration.

Those who have used the disintegration method of obtaining thin metallic films have often observed that the rate of disintegration under ordinary vacuum-tube conditions seems to be inappreciable in the early stages. J. J. Thomson has suggested that discrimination must be made between disintegration of the cathode and disintegration of the gaseous layers of the surface; and some experiments by Hodgson\* also suggest that this apparent delay in disintegration is intimately connected with the evolution of gas from the cathode in the early stages of discharge. An investigation of the effect of previous use of a cathode on its subsequent rate of disintegration seemed, therefore, to be of considerable interest.

\* Hodgson, *Phys. Zeit.* xiii. p. 595 (1912).



A number of similar virgin wires were taken and used as cathodes for varying times. During discharge observations were made on current, cathode, and pressure, and the following facts were very clearly brought out:—

(1) When the discharge is “abnormal”—that is, when the current is greater than that required to cover the cathode with glow—the cathode-fall for constant curve and pressure rises with time; this will be seen on reference to Table I., which shows the results taken with three copper cathodes A, B, and C, at a pressure of 0.20 mm. and a current of 6.15 milliamps.

TABLE I.

Duration of Discharge in minutes.	Cathode Fall.		
	A.	B.	C.
0.1	680	700	770
1.0	680	800	790
2.0	720	780	880
3.0	735	910	990
4.0	880	990	1070
5.0	920	1050	1100
6.0	980	1100	1150
8.0	1060	1150	1210
10.0	1120	1190	1210
15.0		1210	1220
20.0		1280	1330
25.0		1320	1350
30.0		1370	1390

At high currents or cathode-falls, oxidation of cathodes may set in and vitiate the results; but this was not the case in the experiments cited above, the wire presenting a clean surface of pure copper throughout. Moreover, the same effect was observed to a smaller extent with platinum wires. The conclusion is that the cathode-fall, which is an important factor in disintegration work, can only be maintained at a constant value for a constant current by varying the pressure. The problem of the influence of factors on disintegration becomes therefore very complex unless the direct effect of pressure is nil, or at any rate small. Granqvist showed that the rate of disintegration increased rapidly with reduction of pressure, but constant cathode-fall was not maintained in his experiments. Both Kohlschutter and Holborn and Austin have assumed that the direct effect of variation of pressure

is negligible, and this assumption seemed to be justified by some observations by the former on cathodes of different size with which constant current density and cathode-fall were maintained.

The authors have confirmed this in two ways. In the first place observations were made on the changes of pressure during discharge from a given cathode at constant cathode-fall ( $V$ ), current ( $C$ ), and duration ( $t$ ). It was found that the rate of disintegration was independent of the limits between which the pressure varied during discharge. The results taken alone, however, are not conclusive because, owing to the conditions of experiment, the range of pressure variation was necessarily very limited. A typical set of results is given, however, in Table II.

TABLE II.

Platinum Cathode.

 $V=800$ .  $C=3.08$  milliamps.  $t=30$  minutes.

Pressure in mm.		Disintegration in mgs.
Initial.	Final.	
.08	.22	3.5
.08	.27	3.3
.07	.35	3.4
.08	.40	3.5

The strongest evidence, however, is obtained by the second method, in which the duration of the discharge was altered. These experiments are detailed below and show that the direct effect of pressure is negligible over a very wide range.

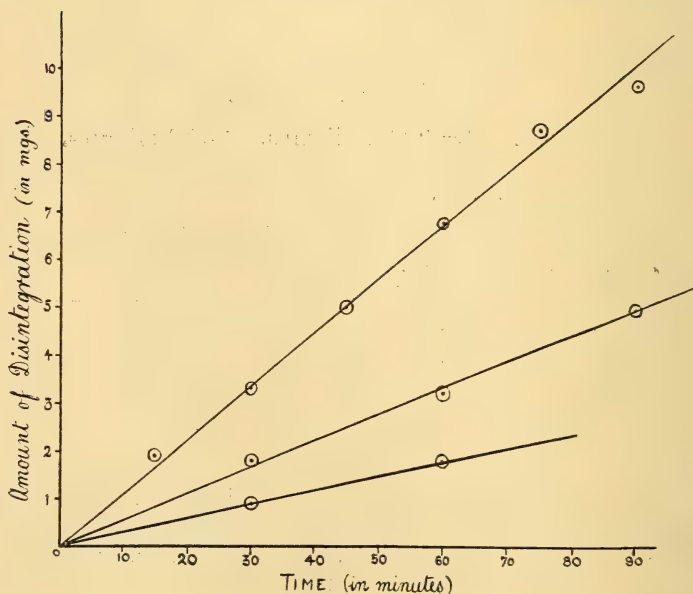
(2) Experiments with both copper and platinum cathodes showed that, provided constant cathode-fall was maintained, the disintegration was the same within the limits of experimental error (*a*) whether the wire had or had not been used previously as a cathode, and (*b*) whether it was discharged from immediately after being placed in the tube or after a long interval *in vacuo*.

(3) As the result of the experiments of (1) and (2) it was

a simple matter to obtain disintegration-time curves for constant current and cathode-fall by varying resistance and pressure accordingly. With copper electrodes the oxidation trouble mentioned above prevented the work being carried very far, and from this point onwards only platinum cathodes were used. Three experiments were carried out with cathode-falls 500, 600, and 800 volts respectively, the current in each case was 3.08 milliamps.

The results given in Curves 1 show conclusively that, provided constant cathode-fall and current are maintained, the rate of disintegration of a given cathode is constant from the commencement of discharge. The apparent lag in the

CURVES 1.



start of disintegration observed in many cases and cited above is thus due to the relatively low value of cathode-fall in the early stages of discharge under ordinary uncontrolled conditions: it must, therefore, be regarded as a secondary effect. In these experiments the pressure change during discharge varied enormously (from 0.05 to 1.72 mm.) for different readings, and the closeness with which the points lie on straight lines may therefore be taken as confirming the conclusions of (1) over a wide range.

*Influence of Cathode Fall of Potential.*

This was first studied in detail by Holborn and Austin, who found that metals could be arranged in two groups for which the disintegration “ $y$ ” expressed in milligrams per half-hour for a current of 0.6 milliampere is given by the expression

$$y = \frac{kA}{n} (V - 495) \times 10^{-2},$$

where  $A$  is the atomic weight, “ $n$ ” the valency, and “ $V$ ” the cathode-fall in volts.  $k$  for air is 0.0016 for the first group and 0.0018 for the second. Kohlschutter has confirmed and extended this work.

Now this result implies that the disintegration is zero when the cathode-fall is 495 volts, and it has been stated that this is borne out by experience\*.

The values at low cathode-falls obtained in previous experiments are meagre in number, but so far as they go they show that the linear relationship breaks down in this region. In any case they have been neglected in enunciating the law. Since, however, considerable importance has been attached to this “limiting” value of cathode-fall, the authors felt that more systematic determinations of disintegration at low values were desirable. This was possible despite the small rate of disintegration in such cases, since for constant fall and current the rate of disintegration is constant, and the discharge could therefore be carried on for long periods of time.

The results for a number of different currents are shown in Curves 2. It will be seen that the relationship between rate of disintegration (ordinates) and cathode-fall (abscissæ) is not linear at low values of the latter: the curves, however, do appear to approach asymptotes which may reasonably cut the horizontal axis at about 500 volts. Thus the rate of disintegration, though small, is appreciable at this value.

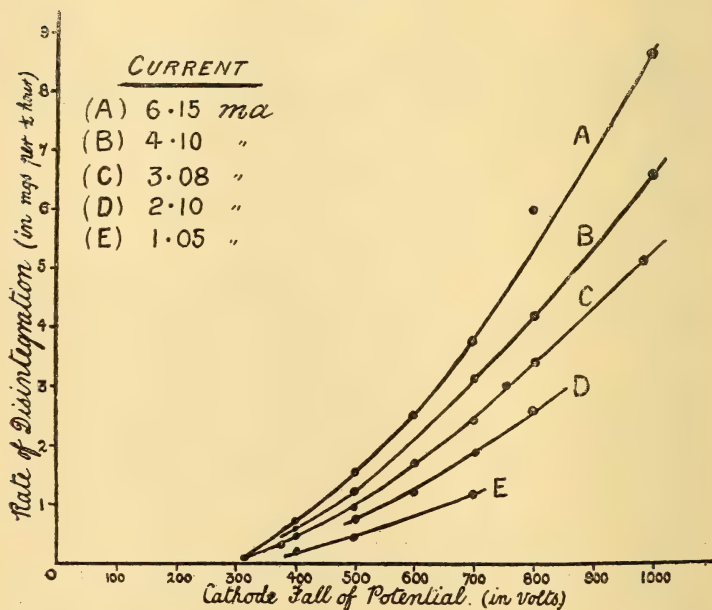
The determination of the true limiting value of “ $V$ ” is a matter of considerable interest. The lowest value of “ $V$ ” obtainable is of course the normal cathode-fall. The apparatus was not suitable for determining the true normal fall accurately, because, except with small currents, the exploring wire had to be placed somewhat close to the cathode. But the conditions were arranged so that the glow covered the cathode but contracted suddenly when the current was slightly reduced; the rate of disintegration was then measured. The reading of the electrometer at the time was generally

\* J. J. Thomson, ‘Rays of Positive Electricity,’ 1914.



about 320–330 volts. It will be seen from the curves 6.15 and 3.08 m.a. that the rate of disintegration at this value of “V” is exceedingly small but not zero. However, until more accurate experiments have been carried out in this region, it may be assumed that the rate of disintegration is zero at or not much below the normal cathode-fall.

CURVES 2.



In order to prove that the form of curves obtained was not due to the particular shape of cathode and discharge-tube used, some of the experiments were repeated with (1) a plate cathode backed by mica as used by Holborn and Austin, and (2) a discharge-tube of spherical form which was a replica of that used by Kohlschutter. The results did not materially differ from those above cited. In the case of the plate cathode, the actual values of disintegration differed from corresponding experiments with wire cathodes by a few per cent., but this difference is easily accounted for by non-uniformity of discharge introduced by the edge of the plate.

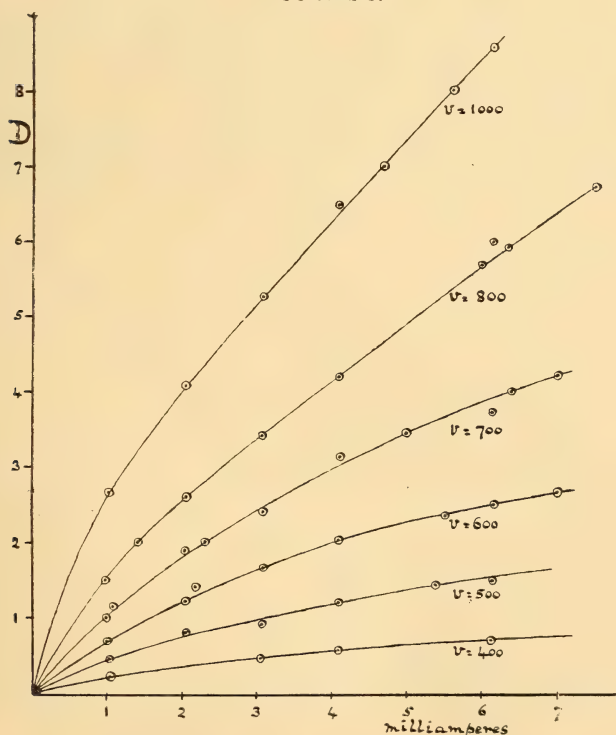
#### *Effect of Current Density.*

The conclusion arrived at by Granqvist that the disintegration for a given cathode is proportional to the square of the current has been somewhat widely quoted. Granqvist,

however, did not work at constant cathode-fall, and moreover, as was first pointed out by Holborn and Austin, his experimental numbers do not give much support to his statement.

Kohlschutter, from the relative slopes of the disintegration-cathode-fall curves at different currents, concluded that the rate of disintegration for a given cathode at constant cathode-fall is proportional to the current. These observations were however, taken with relatively small currents and at high cathode-fall, when the straight-line law between it and disintegration holds good. The authors have shown that in the general case the relationship between disintegration and current is more complex. Curves 3 show the results for

CURVES 3.



a series of determinations with currents ranging from 1 to 7.5 m.a. and cathode-falls from 400 to 1000 volts. The ordinates "D" are values of disintegration in milligrams per half-hour. It is clear from these curves that as the current increases the rate of increase of the disintegration decreases.

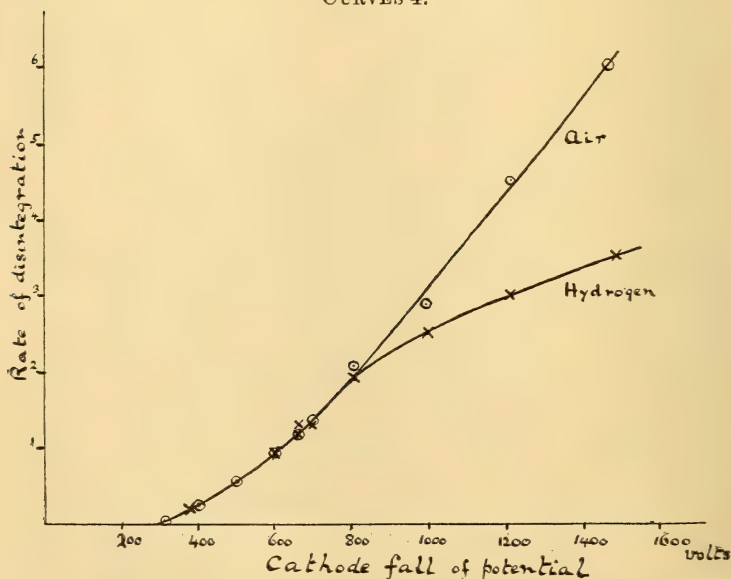
*Influence of the Nature of the Residual Gas.*

It has been shown that the rate of disintegration depends on the nature of residual gas in the tube, certain gases such as argon apparently favouring disintegration, others such as hydrogen retarding it. Kohlschutter is of the opinion that the rate of disintegration increases with the density of the gas.

Now the values of normal cathode-fall in different gases are not in the order of their densities; thus in some recent experiments Rottgardt\* obtained the following values:—Argon, 131 volts; Air, 277 volts; Nitrogen, 216 volts; Hydrogen, 276 volts. But it has been shown above that the disintegration tends to vanish at the normal fall; and if this be so, the statement that the rate of disintegration increases with the density of the gas must break down at low values of cathode-fall. An investigation of rates of disintegration in this region seemed, therefore, desirable.

Only a few preliminary results have so far been obtained, and these in the two gases, air and hydrogen. The hydrogen was prepared by electrolysis and purified by absorption in

CURVES 4.



spongy palladium. The results are shown in Curves 4, in which rate of disintegration (ordinates) is plotted with

\* Rottgardt, *Ann. d. Phys.* xxxiii. p. 1161 (1910).

cathode-fall (abscissæ) for a current of 3.08 milliamps. The values in hydrogen are shown by crosses, and those in air by circles. It will be seen that the effect observed by previous experimenters—namely, that the rate of disintegration in hydrogen is less than that in air—is only true at higher cathode-falls. At low falls a number of measurements failed to show any difference between the rates in air and hydrogen.

This result, if it should prove to hold generally at all currents, is one of considerable interest. It may be noted that the normal cathode-fall is practically the same in air and hydrogen: hence it would be expected that the rates of disintegration would vanish in both gases at the same point. Further, there is reason to believe that the flattening of the hydrogen curve at higher falls is a secondary effect and not necessarily a density effect, because it has been observed by Kohlschutter in nitrogen and oxygen at still higher falls. The experiments are being extended to other gases, particularly argon, and until these have been carried out, any suggestions which are made must be regarded as purely tentative. But the results, so far as they go, suggest that the influence of the nature of the gas may not be a density effect, but may depend on the value of the normal fall coupled with a secondary effect setting in at higher values of cathode-fall. On this view, the favourable influence of argon on disintegration would be due to the low value of normal fall, and the fact that the secondary effect does not occur within the limits of cathode-fall employed. This is further consistent with the fact observed by Kohlschutter, that small traces of impurity added to the pure gases have a marked effect on the rate of disintegration: it is well known that the normal cathode-fall in a gas is influenced in the same way.

In order to test whether the above results in hydrogen were caused by an impurity acquired during the passage of the hydrogen from the palladium to the discharge-tube, some sodium amalgam was placed between them and the hydrogen bubbled through it. No difference could be detected between the measured rate of disintegration in these and previous experiments.

#### *General Considerations.*

The experiments on the early stages of discharge and on the effects of pressure and duration of discharge, show that when a cathode is used which does not oxidize and which is



of low volatility, the phenomenon of disintegration is much simplified and can be readily controlled from the very start of discharge.

It has generally been agreed that the disintegration is caused by positive rays. Thus Stark regards a particle of disintegrated cathode as a secondary "atom-ray," and making certain arbitrary assumptions he has deduced an expression for the velocity of expulsion of such rays. One would expect that the rate of disintegration of a cathode would depend on the number, the energy, and the specific charges of the particles striking it. Now the positive rays are complex in these respects. J. J. Thomson classes under positive rays (a) rays of atomic or molecular size with simple or multiple positive charges and of varying velocity acquired by falling through the whole or part of the Crookes dark space; (b) similar rays, but possessing a constant high velocity uninfluenced by the cathode-fall; (c) uncharged rays also of high velocity. There is no means at present of determining what individual part these different forms play in the production of disintegration, and a theoretical analysis of the curves obtained would therefore be premature.

There is one point, however, which may be noted. In previous discussions on the effect of current density, it has generally been tacitly assumed (1) that all or a constant fraction of the positive rays arriving at the cathode are effective in producing disintegration, and (2) that they carry a constant proportion of the current in the dark space. On the former point there is no information. Some experiments by Hodgson and Mainstone\* on the heating effect of the "normal" discharge at the cathode lend support to the latter assumption; but it is doubtful whether their conclusions can be applied to the above results, because in these the cathode-falls were in general much higher and the cathodes used were very small. Under these conditions much higher temperatures would be obtained, and it might be expected that an increase in cathode-fall or current might cause an increase in the proportion of current carried by negative ions in the dark space. This may explain why the proportionality between current density and rate of disintegration previously observed at small values of current is not maintained in the general case.

It is also interesting to note in this connexion that the marked flattening of the disintegration-cathode-fall curves which sets in at high cathode-falls occurs more readily in hydrogen than in other gases; it is well known that the

\* Phil. Mag. xxvi. p. 411 (1913).

presence of hydrogen facilitates the production of a thermionic current.

The fact that the disintegration vanishes at the normal cathode-fall is one of considerable theoretical interest and importance, but discussion of this and other points is reserved until further data have been obtained.

*Summary.*

Some of the factors which govern the disintegration of a platinum cathode in a vacuum tube have been investigated, with the following results :—

1. *Provided that a constant cathode-fall is maintained :*

(a) Considerable changes in pressure have no influence on the amount of disintegration for a given current and duration of discharge ;

(b) New and old cathodes of the same area disintegrate practically to the same extent under the same conditions of current and duration of discharge ;

(c) The rate of disintegration for a given current density is constant throughout discharge. Thus it is not affected by the removal of gases from the surface of the cathode by previous discharge.

2. The influence of the cathode-fall of potential on the rate of disintegration has been investigated at low values of cathode-fall. No simple relationship (such as exists at high values) has been observed. The rate of disintegration appears to vanish at the normal cathode-fall.

3. The linear relationship which exists between current density and rate of disintegration at small current densities and high cathode-falls does not hold in the general case.

4. Preliminary work on the influence of the nature of the gas shows that at low values of cathode-fall there is no appreciable difference between the rates of disintegration in hydrogen and air under similar conditions.

5. Certain theoretical considerations are advanced in connexion with some of the above results.

The above experiments were carried out in the Physical Laboratory of the University of Bristol. Our thanks are due to Mr. J. R. Boon, B.Sc., who rendered valuable assistance in the observations throughout the latter part of the work. We were further aided in the work by a grant from the Research Fund of the University Colston Society.

January 10th, 1914.

XLVI. *Notes on Electricity and Magnetism.*—1. *The "Rails and Slider" Magneto-machine.* 2. *Permanent Magnets and Dynamical Theory.* By Professor A. GRAY, F.R.S.\*

EVERYONE knows the arrangement of rails and sliding bar in a uniform magnetic field which constitutes the simple magneto-machine devised in 1863, or thereabouts, by Lord Kelvin to illustrate the dimensions (first pointed out I believe by Wilhelm Weber) of electric resistance in the ordinary electromagnetic system of units. The first account of it, so far as I am aware, is in the 1863 Report of the B. A. Committee on Electrical Standards, where it appears twice, first in the general part of the Report, and again in § 30 of the Appendix on "Elementary Relations between Electrical Measurements," which was drawn up by Clerk Maxwell and Fleeming Jenkin. It is very curious that in these first statements of the action of the machine, and all later discussions of it (including my own) which I have seen, the theory given is imperfect in one important respect †. No mention whatever is made of the self-inductance of the circuit; and it does not seem possible by any special arrangement of the conductors to make the self-inductance remain zero or constant as the slider moves. In the references to the arrangement in Maxwell's 'Electricity,' §§ 594, 595, 596, the question of self-inductance does not arise.

At the date mentioned self-inductance was no doubt much less in the minds of electricians than it is now. For example, though it plays no part in the mathematical theory of current induction sketched by Helmholtz in 1847, in his famous essay "Die Erhaltung der Kraft," its existence had been fully established by Faraday's experiments ('Experimental Researches,' § 1090, &c.); and it was the great feature of Thomson's paper published in this Journal in 1853, that the term  $\frac{1}{2}L\gamma^2$  in the electrokinetic energy of a circuit (explicitly pointed out in a previous paper "On the Mechanical Values of Distributions of Electricity, Magnetism, and Galvanism," communicated to the Glasgow Philosophical Society in January of that year) is applied to the explanation of the oscillatory discharge of a condenser through a coil of wire connecting its plates. Here the self-inductance appears under the name of "Electromagnetic Inertia," which very clearly indicates its dynamical significance.

\* Communicated by the Author.

† (Note added Feb. 12.) Professor Carey Foster has kindly called my attention to the fact that the omission is noticed in his and Prof. Porter's 'Electricity and Magnetism,' editions 1909, 1913, § 299.



In the usual presentation of the rails and slider illustration the sliding bar has length  $l$  between the rails, which are laid in a magnetic field of uniform intensity  $H$ , so that the bar, moving with speed  $v$  in a direction at right angles to its length, cuts perpendicularly across the lines of force of the impressed field. The rails are connected by a wire so that the total resistance of the circuit is  $R$ ; and for simplicity the rails and slider are regarded as being of negligible resistance, so that  $R$  may be taken as practically all contained in the wire. It is explicitly assumed (*B. A. Rep. loc. cit.*) that the speed  $v$  of the slider and the current produced by the motion are both constant. The following investigation will show that this assumption is untenable.

The applied electromotive force in the circuit is  $Hlv$ , due we suppose to motion of the slider caused by an external agent acting against the electromagnetic forces applied to the bar; and, if we suppose the self-inductance at a given instant to be  $L$ , and the current  $\gamma$  to be constant, the equation of motion is

$$Hlv - \dot{L}\gamma = R\gamma, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

since clearly as the slider moves  $L$  must vary. The condition that  $\gamma$  is constant gives also

$$H\dot{v} = \ddot{L}\gamma. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The rate at which work is done on the slider by an external agent is  $Hlv\gamma$ , and this is spent in the rates  $\frac{1}{2}\dot{L}\gamma^2$ , at which the electrokinetic energy  $\frac{1}{2}L\gamma^2$  is increased,  $R\gamma^2$  at which heat is produced in the circuit, and the rate  $mv\dot{v}$  at which the kinetic energy  $\frac{1}{2}mv^2$  of the sliding bar is added to. Thus we obtain

$$Hlv\gamma = mv\dot{v} + \frac{1}{2}\dot{L}\gamma^2 + R\gamma^2. \quad . \quad . \quad . \quad . \quad (3)$$

To make the equations quite general we might have included the effect of a motor (or its equivalent in the form of electrolytic cells, or the like) in the circuit. If  $E$  be the back-electromotive force of such an arrangement, due to the performance of work otherwise than in the direct production of heat, equation (1) becomes

$$Hlv - \dot{L}\gamma = E + R\gamma; \quad . \quad . \quad . \quad . \quad (4)$$

and instead of (3) we have

$$Hlv\gamma = mv\dot{v} + \frac{1}{2}\dot{L}\gamma^2 + E\gamma + R\gamma^2, \quad . \quad . \quad . \quad (5)$$

where  $R$  is the total resistance in circuit.



Multiplying (4) by  $\gamma$  and subtracting from (5) we get

$$mv\dot{v} = \frac{1}{2}\dot{L}\gamma^2; \quad . \quad . \quad . \quad . \quad . \quad (6)$$

so that the time-rate of increase of the kinetic energy of the slider is equal to the rate of increase of the electrokinetic energy.

This is of course in accordance with the theorem given by Lord Kelvin in 1851 (*Electr. and Mag.* 2nd ed. p. 446) with regard to the work done in two mutually influencing circuits, the conductors of which are brought to rest by externally applied forces.

It may be noticed that (6) may be obtained at once from the expression for the whole kinetic energy

$$\frac{1}{2}L\gamma^2 + \frac{1}{2}m\dot{x}^2$$

(where  $\dot{x}=v$ ) by the Lagrangian method. For we have then

$$m\ddot{x} - \frac{1}{2}\gamma^2 \frac{dL}{dx} = 0,$$

or

$$m\dot{x}\ddot{x} - \frac{1}{2}\dot{L}\gamma^2 = 0,$$

which is (6).

Now the self-inductance of the rails regarded as direct and return wires of circular section connected by the slider at one end can easily be found. If  $x$  be the length of rail from the slider to the points of attachment of the wire,  $\rho$  the radius of each wire,  $l$  the distance apart of the axes of the wires, and the magnetic inductivity be taken as unity everywhere (wires made of copper, for example), the self-inductance is given by

$$L = 4x \left( \log \frac{l}{\rho} + \frac{1}{4} \right) - 4l + \text{terms depending on the rail cross-connections.}$$

Hence we have

$$\frac{dL}{dx} = 4 \log \frac{l}{\rho} + 1,$$

or

$$\frac{dL}{dt} = \frac{dL}{dx} \dot{x} = \left( 4 \log \frac{l}{\rho} + 1 \right) v. \quad . \quad . \quad (7)$$

Now we have seen that  $mv\dot{v} = \frac{1}{2}\dot{L}\gamma^2$ , so that from (6) and (7) we obtain

$$mv\dot{v} = \frac{1}{2} \left( 4 \log \frac{l}{\rho} + 1 \right) \gamma^2 v, \quad . \quad . \quad . \quad . \quad (8)$$

and therefore, if  $v=v_0$  at time  $t_0$ ,

$$\frac{1}{2}m(v^2 - v_0^2) = \frac{1}{2}\gamma^2 \left( 4 \log \frac{l}{\rho} + 1 \right) s, \quad . \quad . \quad . \quad (9)$$

where  $s$  is the distance traversed by the slider in time  $t-t_0$ .

But we have also

$$\dot{v} = \frac{\gamma^2}{2m} \left( 4 \log \frac{l}{\rho} + 1 \right); \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and therefore

$$v - v_0 = \frac{\gamma^2}{2m} \left( 4 \log \frac{l}{\rho} + 1 \right) (t - t_0); \quad . \quad . \quad . \quad . \quad (11)$$

and

$$s = v_0(t - t_0) + \frac{\gamma^2}{4m} \left( 4 \log \frac{l}{\rho} + 1 \right) (t - t_0)^2. \quad (12)$$

Hence we can write (9) in the form

$$\frac{1}{2}m(v^2 - v_0^2) = \frac{1}{2}\gamma^2 \left( 4 \log \frac{l}{\rho} + 1 \right) (t - t_0) \left\{ v_0 + \frac{\gamma^2}{4m} \left( 4 \log \frac{l}{\rho} + 1 \right) (t - t_0) \right\}. \quad (13)$$

We have also 
$$L - L_0 = \left( 4 \log \frac{l}{\rho} + 1 \right) s. \quad . \quad . \quad . \quad (14)$$

The rails and slider illustration though apparently very simple is not really so, and is inferior to the arrangement, sometimes substituted, of a metal disk rotating across the lines of force of an impressed magnetic field, and touched at its centre and circumference, or at the circumference and at some concentric circle nearer the centre, by the terminals of the external part of the circuit. If the field be maintained constant and the disk rotate at a uniform rate, and there be no variation of contacts of the wire with the disk, a constant current will be maintained. This of course is the arrangement of a disk magneto-machine, and of the Lorenz apparatus for the determination of the ohm, except that in the latter case the electromotive force in the disk circuit is balanced.

In this arrangement there is no change of self-induction, inasmuch as the configuration remains unchanged as the rotation proceeds. For total magnetic induction,  $I$ , through the area of the disk between the circles of contact, and angular speed  $\omega$ , the electromotive force is  $I\omega/2\pi$ . If the field be of uniform intensity  $H$ , and  $a, a'$  be the radii of the circles of contact, the value of  $I$  is  $\pi(a^2 - a'^2)H$  and the electromotive

force is  $\frac{1}{2}(\alpha^2 - \alpha'^2)H\omega$ . The current is  $I\omega/2\pi R$ , and is constant.

2. The conclusion (see Lord Kelvin's 'Electrostatics and Magnetism,' § 571, *note*) that the "mechanical value" of a current in a closed conductor is not affected by steel magnets in the neighbourhood, has always seemed to me remarkable and significant. For it would appear that we must, if we assume the Amperean hypothesis that a permanent magnet is made up of a congeries of circuits of molecular dimensions, in which currents of electricity circulate, introduce a term of the form  $M\gamma'\gamma$ , or rather a sum  $\gamma\Sigma(M\gamma')$  of such terms, to express the mutual energy of the circuit carrying the current  $\gamma$  and the multitude of molecular currents typified by  $\gamma'$ . Thus if we write for the total kinetic energy (electrokinetic and ordinary kinetic energy, taken together)

$$T = \frac{1}{2}\{L\gamma^2 + \Sigma L'\gamma'^2 + 2\gamma\Sigma(M\gamma') + \Sigma(mv^2)\}, \quad (1)$$

we should obtain from this and the molar potential energy, by the Lagrangian method, the equations of motion, as we may call them, both of electricity and of molar matter.

Thus for the rails and slider we should get, bringing in the dissipation function,  $\frac{1}{2}R\gamma^2$ , the equations

$$\left. \begin{aligned} -\frac{d}{dt}\{L\gamma + \Sigma(M\gamma')\} &= R\gamma, \\ mv\dot{v} - \dot{L}\gamma &= 0, \end{aligned} \right\} \dots \dots (2)$$

since we suppose  $\gamma$  to be constant.

Here we identify  $-\Sigma\dot{M}\gamma'$  with  $Hlv$  and obtain

$$Hlv - \dot{L}\gamma = R\gamma, \dots \dots (3)$$

and so far there is no difficulty about the mutual term  $\gamma\Sigma(M\gamma')$ .

Let us now consider any number of battery circuits in the field of a system of permanent magnets. Let  $E_1, R_1, L_1, \gamma_1$ , be the electromotive force, the resistance, the self-inductance, and the current for one battery circuit,  $E_2, R_2, L_2, \gamma_2$  those for another, and so on. Considering the magnets as assemblages of molecular circuits, and denoting by  $T$  as before the whole kinetic energy (that is  $T_e + T_m$  the sum of the electrokinetic energy and the molar kinetic energy of moving conductors), and by  $x_1, x_2, \dots$  coordinates determining the configuration of the conductors, we can write the equations

of the circuits and of the moving parts of the systems in the two sets

$$\left. \begin{aligned} \frac{d}{dt} \frac{\partial T}{\partial \gamma_1} &= E_1 - R_1 \gamma_1 \\ \frac{d}{dt} \frac{\partial T}{\partial \gamma_2} &= E_2 - R_2 \gamma_2 \\ \cdot &\cdot \cdot \cdot \cdot \cdot \cdot \\ \frac{d}{dt} \frac{\partial T}{\partial \gamma_1'} &= 0 \\ \frac{d}{dt} \frac{\partial T}{\partial \gamma_2'} &= 0 \\ \cdot &\cdot \cdot \cdot \cdot \cdot \cdot \end{aligned} \right\} \cdot \cdot \cdot \cdot \cdot \cdot \quad (4)$$

$$\left. \begin{aligned} \frac{d}{dt} \frac{\partial T}{\partial \dot{x}_1} - \frac{\partial T}{\partial x_1} &= 0 \\ \frac{d}{dt} \frac{\partial T}{\partial \dot{x}_2} - \frac{\partial T}{\partial x_2} &= 0 \\ \cdot &\cdot \cdot \cdot \cdot \cdot \cdot \end{aligned} \right\} \cdot \cdot \cdot \cdot \cdot \cdot \quad (5)$$

Here we suppose that only internal electromagnetic forces  $\partial T / \partial x_1, \partial T / \partial x_2, \dots$ , act on the system, and that there is no ordinary dynamical force on the matter of the system. There is no difficulty about including such forces as the latter; but the object at present is to obtain as simple as possible a statement of the theory of a number of circuits under their mutual action alone. Also it is assumed that there are in the kinetic energy no terms involving products of the form  $\gamma \dot{x}$ . See Maxwell, 'Electricity,' § 574.

Multiplying equations (4) in order by  $\gamma_1, \gamma_2, \dots, \gamma_1', \gamma_2' \dots$ , and the second set in order by  $\dot{x}_1, \dot{x}_2, \dots$ , and adding, we get for the interval of time  $dt$ , the equation

$$dT = dT_e + dT_m = \Sigma (E\gamma - R\gamma^2) dt. \quad \cdot \cdot \cdot \quad (6)$$

But the second set of equations (5) taken by itself gives (since

$$\Sigma \left( \dot{x} \frac{d}{dt} \frac{\partial T}{\partial \dot{x}} \right) = \Sigma (m \dot{x} \ddot{x}),$$

and the work  $dW$  done by the electromagnetic forces  $\partial T / \partial x_1, \dots$ , is given by

$$dW = \Sigma \left( \dot{x} \frac{\partial T}{\partial x} \right) dt,$$

the relation

$$dT_m = dW. \quad \cdot \cdot \cdot \cdot \cdot \cdot \quad (7)$$

Hence we have

$$dT_e + dW = \Sigma (E\gamma - R\gamma^2) dt. \quad \cdot \cdot \cdot \quad (8)$$



Thus the batteries furnish in time  $dt$  a quantity of energy, over and above that converted into heat, equal to the increment of electrokinetic energy and the work done by the electromagnetic forces, taken together.

Let us now consider the effect of a change of configuration of the battery circuits, without change of the currents in these circuits, that is allow the steady state to have been resumed before the effect on the magnets is estimated. Thus in  $dT_e$  we have no terms depending on  $d\gamma_1, d\gamma_2, \dots$ . But inasmuch as the mutual inductances between each of the battery circuits and the various molecular circuits are, we suppose, altered by change of configuration, and there is electromotive force of induction but no resistance in any molecular circuit, we have, not merely in the present case but always,

$$\frac{d}{dt} \sum \{L'\gamma' + \sum (M\gamma)\} = 0. \quad . \quad . \quad . \quad (9)$$

Here one summation, the inner, is taken for all the battery circuits (carrying current  $\gamma$ ) and the other for all the molecular circuits.

If the currents  $\gamma$  be of moderate amount only very small changes, if any, are produced by the changes of configuration—this is matter of observation. In considering, however, the influence of the presence of the magnets on the dynamical value of the system, we have to take the effect, not of moving the conductors in the field, but of opening the circuits while fixed in position. When this is done the effect if any of the annulment of the terms  $\sum \sum (M\gamma\gamma')$  is to be traced in change of the magnets. For when the circuits are opened the tubes of magnetic induction through the circuits produced by the magnets are not changed (except in so far as the magnets are changed by the withdrawal of the tubes thrust through the molecular circuits by the battery circuits), they remain *in situ*, none of them crosses the wires. On the other hand, the tubes which the battery circuits have linked through the molecular circuits shrink in and disappear, and cross these latter circuits in doing so. On this view the effect of the evanescence of the terms  $\sum \sum (M\gamma\gamma')$ , in these circumstances, ought to be looked for in the magnets.

From (9) we obtain by integration

$$\sum \{L'\gamma' + \sum (M\gamma)\} = \sum (L'\gamma'_0),$$

where  $\gamma'_0$  denotes the current in a molecular circuit when the currents  $\gamma$  have ceased to exist.

If practically no change takes place in the molecular

currents we must have  $\Sigma\Sigma(M\gamma)$  small in comparison with  $\Sigma(L'\gamma')$ . This would make any change that can occur in a  $\gamma'$ , in consequence of opening the battery circuits, a small quantity of the order of  $M\gamma$  in magnitude. In this case the dynamical value of a current in a conductor would not be appreciably affected by the presence of permanent magnets in its neighbourhood.

The number of molecular circuits in an ordinary magnet must, if the Amperean theory be true, be exceedingly great. Let a uniformly magnetized filament be illustrated by a solenoid made up of a very large number of equal distinct circuits in each of which a current  $\gamma'$  flows. If the number of circuits per unit length be  $n$ , and the area of each be  $A$ , the value of the aggregate self-inductance,  $L'$  say, is  $4\pi n^2 l A$ , where  $l$  is the length of the solenoid, and the total induction through it (neglecting the ends) is  $4\pi n^2 l A \gamma'$ , for current  $\gamma'$  in each turn. Now let a circuit carrying the current  $\gamma$  be wrapped close round the solenoid in  $n'$  turns. The mutual induction will be at most  $4\pi n n' \gamma A$ . Thus we have  $M/L' = n'/nl$ . This ratio will for a magnet be exceedingly small, and thus, unless  $\gamma/\gamma'$  be very great, the condition stated above will be fulfilled.

The discrepancy set up by the dynamical theory is on these suppositions only apparent, and the Amperean theory does not seem incompatible with the unity of explanation of magnetic phenomena, which is a requisite of every explanation of permanent magnetism. This kind of onesidedness of result if it really exists has a bearing on the question of relativity, and it seems desirable to examine the different cases in detail.

As was pointed out by Maxwell ('Elect. and Mag.' vol. ii. § 844) it is necessary in order that the Amperean currents may give an inductive magnetization agreeing with experiment, that the self-inductance of each molecular current be great, that is  $A/L'$  must be small. This is also in accordance with the conclusion come to above. If the current flow in a ring-channel this condition, as Maxwell states, may be fulfilled by means of a radius  $R$  of the mean line of the channel great in comparison with the radius  $r$  of the channel, since  $L'$  depends on  $\log(R/r)$ .

I reserve some further discussion of this subject, from the point of view of an electron-theory of magnetism, for another opportunity.

XLVII. *Further Calculations concerning the Momentum of Progressive Waves.* By Lord RAYLEIGH, O.M., F.R.S.\*

THE question of the momentum of waves in fluid is of interest and has given rise to some difference of opinion. In a paper published several years ago † I gave an approximate treatment of some problems of this kind. For a fluid moving in one dimension for which the relation between pressure and density is expressed by

$$p = f(\rho), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

it appeared that the momentum of a progressive wave of mean density equal to that of the undisturbed fluid is given by

$$\left\{ \frac{\rho_0 f''(\rho_0)}{4a^3} + \frac{1}{2a} \right\} \times \text{total energy}, \quad . \quad . \quad . \quad (2)$$

in which  $\rho_0$  is the undisturbed density and  $a$  the velocity of propagation. The momentum is reckoned positive when it is in the direction of wave-propagation.

For the "adiabatic" law, viz. :

$$p/p_0 = (\rho/\rho_0)^\gamma, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$f'(\rho_0) = \frac{\gamma p_0}{\rho_0} = a^2, \quad f''(\rho_0) = \frac{p_0 \gamma (\gamma - 1)}{\rho_0^2}, \quad . \quad . \quad (4)$$

so that

$$\frac{\rho_0 f''(\rho_0)}{4a^3} + \frac{1}{2a} = \frac{\gamma + 1}{4a}. \quad . \quad . \quad . \quad . \quad (5)$$

In the case of Boyle's law we have merely to make  $\gamma = 1$  in (5).

For ordinary gases  $\gamma > 1$  and the momentum is positive; but the above argument applies to all positive values of  $\gamma$ . If  $\gamma$  be negative, the pressure would increase as the density decreases, and the fluid would be essentially unstable.

However, a slightly modified form of (3) allows the exponent to be negative. If we take

$$p/p_0 = 2 - (\rho/\rho_0)^{-\beta} \quad . \quad . \quad . \quad . \quad (6)$$

with  $\beta$  positive, we get as above

$$f'(\rho_0) = \frac{\beta p_0}{\rho_0} = a^2, \quad f''(\rho_0) = -\frac{(\beta + 1)a^2}{\rho_0}, \quad . \quad (7)$$

and accordingly

$$\frac{\rho_0 f''(\rho_0)}{4a^3} + \frac{1}{2a} = \frac{1 - \beta}{4a}. \quad . \quad . \quad . \quad . \quad (8)$$

\* Communicated by the Author.

† Phil. Mag. vol. x. p. 364 (1905); Scientific Papers, vol. v. p. 265.

If  $\beta=1$ , the law of pressure is that under which waves can be propagated without a change of type, and we see that the momentum is zero. In general, the momentum is positive or negative according as  $\beta$  is less or greater than 1.

In the above formula (2) the calculation is approximate only, powers of the disturbance above the *second* being neglected. In the present note it is proposed to determine the sign of the momentum under the laws (3) and (6) more generally and further to extend the calculations to waves in a liquid moving in two dimensions under gravity.

It should be clearly understood that the discussion relates to *progressive* waves. If this restriction be dispensed with, it would always be possible to have a disturbance (limited if we please to a finite length) without momentum, as could be effected very simply by beginning with displacements unaccompanied by velocities. And the disturbance, considered as a whole, can never acquire (or lose) momentum. In order that a wave may be progressive in one direction only, a relation must subsist between the velocity and density at every point. In the case of Boyle's law this relation, first given by De Morgan \*, is

$$u = a \log (\rho / \rho_0), \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and more generally †

$$u = \int \sqrt{\left(\frac{dp}{d\rho}\right)} \cdot \frac{d\rho}{\rho} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Wherever this relation is violated, a wave emerges travelling in the negative direction.

For the adiabatic law (3), (10) gives

$$u = \frac{2a}{\gamma-1} \left\{ \left(\frac{\rho}{\rho_0}\right)^{\frac{\gamma-1}{2}} - 1 \right\}, \quad . \quad . \quad . \quad . \quad (11)$$

$a$  being the velocity of infinitely small disturbances, and this reduces to (9) when  $\gamma=1$ . Whether  $\gamma$  be greater or less than 1,  $u$  is positive when  $\rho$  exceeds  $\rho_0$ . Similarly if the law of pressure be that expressed in (6),

$$u = \frac{2a}{\beta+1} \left\{ 1 - \left(\frac{\rho}{\rho_0}\right)^{-\frac{\beta+1}{2}} \right\}. \quad . \quad . \quad . \quad . \quad (12)$$

Since  $\beta$  is positive, values of  $\rho$  greater than  $\rho_0$  are here also accompanied by positive values of  $u$ .

\* Airy, Phil. Mag. vol. xxxiv. p. 402 (1849).

† Earnshaw, Phil. Trans. 1859, p. 146.



By definition the momentum of the wave, whose length may be supposed to be limited, is per unit of cross-section

$$\int \rho u \, dx, \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

the integration extending over the whole length of the wave. If we introduce the value of  $u$  given in (11), we get

$$(13) = \frac{2\rho_0 a}{\gamma - 1} \int \left\{ \left( \frac{\rho}{\rho_0} \right)^{\frac{\gamma+1}{2}} - \frac{\rho}{\rho_0} \right\} dx; \quad . \quad . \quad (14)$$

and the question to be examined is the sign of (14). For brevity we may write unity in place of  $\rho_0$ , and we suppose that the wave is such that its mean density is equal to that of the undisturbed fluid, so that  $\int \rho \, dx = l$ , where  $l$  is the length of the wave. If  $l$  be divided into  $n$  equal parts, then when  $n$  is great enough the integral may be represented by the sum

$$\left\{ \rho_1^{\frac{\gamma+1}{2}} + \rho_2^{\frac{\gamma+1}{2}} + \rho_3^{\frac{\gamma+1}{2}} + \dots - \rho_1 - \rho_2 - \dots \right\} \frac{l}{n}, \quad (15)$$

in which all the  $\rho$ 's are positive. Now it is a proposition in Algebra that

$$\frac{\rho_1^{\frac{\gamma+1}{2}} + \rho_2^{\frac{\gamma+1}{2}} + \dots}{n} > \left( \frac{\rho_1 + \rho_2 + \dots}{n} \right)^{\frac{\gamma+1}{2}}$$

when  $\frac{1}{2}(\gamma+1)$  is negative, or positive and greater than unity; but that the reverse holds when  $\frac{1}{2}(\gamma+1)$  is positive and less than unity. Of course the inequality becomes an equality when all the  $n$  quantities are equal. In the present application the sum of the  $\rho$ 's is  $n$ , and under the adiabatic law (3),  $\gamma$  and  $\frac{1}{2}(\gamma+1)$  are positive. Hence (15) is positive or negative according as  $\frac{1}{2}(\gamma+1)$  is greater or less than unity, viz., according as  $\gamma$  is greater or less than unity. In either case the momentum represented by (13) is *positive*, and the conclusion is not limited to the supposition of small disturbances.

In like manner if the law of pressure be that expressed in (6), we get from (12)

$$(13) = \frac{2\rho_0 a}{\beta + 1} \int \left\{ \frac{\rho}{\rho_0} - \left( \frac{\rho}{\rho_0} \right)^{-\frac{\beta-1}{2}} \right\} dx, \quad . \quad . \quad (16)$$

from which we deduce almost exactly as before that the momentum (13) is positive if  $\beta$  (being positive) is less than 1

and negative if  $\beta$  is greater than 1. If  $\beta=1$ , the momentum vanishes. The conclusions formerly obtained on the supposition of small disturbances are thus extended.

We will now discuss the momentum in certain cases of fluid motion under gravity. The simplest is that of *long* waves in a uniform canal. If  $\eta$  be the (small) elevation at any point  $x$  measured in the direction of the length of the canal and  $u$  the corresponding fluid velocity parallel to  $x$ , which is uniform over the section, the dynamical equation is\*

$$\frac{du}{dt} = -g \frac{d\eta}{dx} \quad . \quad . \quad . \quad . \quad . \quad (17)$$

As is well known, long waves of small elevation are propagated without change of form. If  $c$  be the velocity of propagation, a positive wave may be represented by

$$\eta = F(ct - x), \quad . \quad . \quad . \quad . \quad . \quad (18)$$

where  $F$  denotes an arbitrary function, and  $c$  is related to the depth  $h_0$  according to

$$c^2 = gh_0. \quad . \quad . \quad . \quad . \quad . \quad (19)$$

From (17), (18)

$$u = \frac{g\eta}{c} = \sqrt{\left(\frac{g}{h_0}\right)} \cdot \eta \quad . \quad . \quad . \quad . \quad (20)$$

is the relation obtaining between the velocity and elevation at any place in a positive progressive wave of small elevation.

Equation (20), however, does not suffice for our present purpose. We may extend it by the consideration that in a long wave of finite disturbance the elevation and velocity may be taken as relative to the neighbouring parts of the wave. Thus, writing  $du$  for  $u$  and  $dh$  for  $h_0$ , so that  $\eta = dh$ , we have

$$du = \sqrt{\left(\frac{g}{h}\right)} dh,$$

and on integration

$$u = 2\sqrt{g} \{ h^{\frac{1}{2}} + C \}.$$

The arbitrary constant of integration is determined by the fact that outside the wave  $u=0$  when  $h=h_0$ , whence and replacing  $h$  by  $h_0 + \eta$ , we get

$$u = 2\sqrt{g} \{ \sqrt{(h_0 + \eta)} - \sqrt{h_0} \}, \quad . \quad . \quad . \quad (21)$$

\* Lamb's Hydrodynamics, § 168.

as the generalized form of (20). It is equivalent to a relation given first in another notation by De Morgan \*, and it may be regarded as the condition which must be satisfied if the emergence of a negative wave is to be obviated.

We are now prepared to calculate the momentum. For a wave in which the mean elevation is zero, the momentum corresponding to unit horizontal breadth is

$$\rho \int u(h_0 + \eta) dx = \frac{3}{4} \rho \sqrt{g/h_0} \int \eta^2 dx, \quad \dots (22)$$

when we omit cubes and higher powers of  $\eta$ . We may write (22) also in the form

$$\text{Momentum} = \frac{3}{4} \frac{\text{Total Energy}}{c}, \quad \dots (23)$$

$c$  being the velocity of propagation of waves of small elevation.

As in (14), with  $\gamma$  equal to 2, we may prove that the momentum is positive without restriction upon the value of  $\eta$ .

As another example, periodic waves moving on the surface of deep water may also be referred to. The momentum of such waves has been calculated by Lamb †, on the basis of Stokes' second approximation. It appears that the momentum per wave-length and per unit width perpendicular to the plane of motion is

$$\pi \rho a^2 c, \quad \dots (24)$$

where  $c$  is the velocity of propagation of the waves in question and the wave form is approximately

$$\eta = a \cos \frac{2\pi}{\lambda} (ct - x) \quad \dots (25)$$

The forward velocity of the surface layers was remarked by Stokes. For a simple view of the matter reference may be made also to Phil. Mag. vol. i. p. 257 (1876) ; Scientific Papers, vol. i. p. 263.

\* Airy, Phil. Mag. vol. xxxiv. p. 402 (1849).

† Hydrodynamics, § 246.

XLVIII. *The Expression for the Electrical Conductivity of Metals as deduced from the Electron Theory.* By W. F. G. SWANN, D.Sc., A.R.C.S., Assistant Lecturer in Physics at the University of Sheffield\*.

*Introduction.*

THE theory of the electrical conductivity of metals has been worked out on many assumptions. One of the simplest and best known of these methods is that employed by Drude, in which the assumption is made that in the absence of the electric field all the electrons move with the same velocity, and that the velocity produced by the field in an electron is the velocity which is produced in it while it is travelling between two points of collision, the essential assumption being that at each collision the effect of all previous actions of the field on the electron are wiped out. The value of the conductivity  $\sigma$  which has been deduced from these assumptions is

$$\sigma = \frac{ne^2\lambda v}{4\alpha\theta} \dagger, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $n$  is the number of electrons per c.c.,  $\lambda$  is the mean free path,  $v$  is the velocity, and  $\alpha\theta$  is the kinetic energy of a gas molecule at a temperature  $\theta$ .

The object of Part I. of the present paper is to show that the above assumptions do not lead to (1), but to the formula

$$\sigma = \frac{ne^2\lambda v}{3\alpha\theta} . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The difference between (1) and (2) is partly due to what is, in the opinion of the author, an improper use of the quantity known as the mean free path, and partly due to another cause which will be better understood at a later stage of the paper.

The thermal conductivity  $k$  calculated with the proper use of the mean free path gives, for the above case, the ordinarily accepted value  $k = \frac{1}{3}n\lambda v\alpha$ ; and the interesting point is, that while at  $0^\circ$  C. (1) gives  $k/\sigma = 6.3 \times 10^{10}$ , (2) results in  $k/\sigma = 4.7 \times 10^{10}$ . The experimentally found value of  $k/\sigma$  for most pure metals is about  $6.3 \times 10^{10}$  at  $0^\circ$  C.; so that the conclusion to be drawn is, that the assumptions on which (1) and (2) are based are nothing like as representative of the

\* Communicated by the Author (now of the Carnegie Institution of Washington).

† J. J. Thomson, 'Corpuscular Theory of Matter,' p. 56.



facts, even in the matter of the relation between the thermal and electrical conductivity, as has formerly been supposed. The method adopted by Lorentz, Richardson, and others, in calculating the conductivity are based on quite different principles to that adopted in calculating (1) and (2), the persistence of the velocities playing, at any rate implicitly, a primary part in the development of the theories. The value

obtained by Lorentz for  $\sigma$  is  $\sqrt{\frac{2}{3\pi} \frac{ne^2\lambda u}{\alpha\theta}}$ , where  $u$  is here the square root of the mean square velocity. The point of the present paper is not necessarily to suggest that (1) is far wrong in itself, but that the assumptions on which it is based do not lead to it but to (2).

It is perhaps worth while here uttering a word of warning against any feeling which one may have towards assuming that since all methods of calculating the conductivity lead to  $\frac{ne^2\lambda u}{\alpha\theta}$  multiplied by some numerical factor, therefore the assumptions employed in these methods are all more or less equivalent. If we set out on any hypothesis to calculate  $\sigma$  in terms of  $n, e, \lambda, u, \alpha\theta$ , we are practically bound to find  $\frac{ne^2\lambda u}{\alpha\theta}$  multiplied by a numerical factor, since this is practically the only way in which these quantities can be combined so as to result in the dimensions of a conductivity, unless we make some most improbable combinations. When we set out to calculate  $\sigma$  in terms of  $n, e, \lambda, u, \alpha\theta$  the  $\frac{ne^2\lambda u}{\alpha\theta}$  part is little more than the result of pure algebra, so that it would be obtained if all the physics and all the dynamical principles in our arguments were wrong. The correctness of the numerical factor is in fact the only criterion for the truth of the theory.

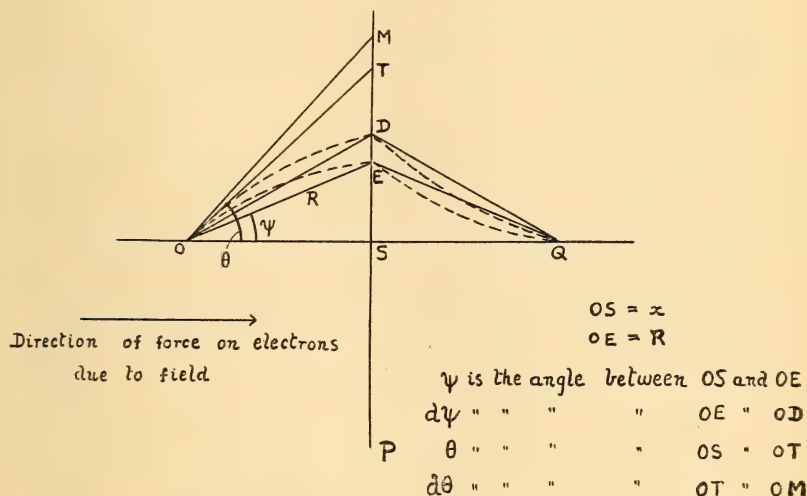
It will be convenient first to give the formal proof of (2), and then to put the proof into such a form as to indicate the exact points in which the discrepancy between (1) and (2) has arisen. One or two mathematical details will be relegated to an appendix.

In Part II. of the paper expressions are deduced for the electrical and thermal conductivities on the same assumptions as those on which (2) is deduced, with the exception that the electrons are supposed to move in the absence of the field with the velocities given by Maxwell's law. A method of improving the theoretical value of  $k/\sigma$  by making the free path a suitable function of the velocity is also discussed.

PART I.—*Deduction of the expression*  $\sigma = \frac{ne^2\lambda\nu}{3\alpha\theta}$ .

Let OS (fig. 1) represent the axis of  $x$ , and let the field  $X$  act from right to left so that the electrons are urged from left to right. We shall proceed to find the flow per square centimetre through the plane perpendicular to the paper and represented by the line MP.

Fig. 1.



If  $\phi$  is measured about OS in the plane perpendicular to the paper, the number  $\Delta n$  of electrons starting out from an element  $d\omega$  at O having suffered collisions therein, and which are contained within the solid angle  $\sin \theta \, d\theta \, d\phi$  is

$$\Delta n = \frac{nv}{4\pi\lambda} \sin \theta \, d\theta \, d\phi \, d\omega,$$

where  $\theta$  is the angle between OS and the radius vector OT drawn from O,  $\lambda$  is the mean free path, and  $v$  is the velocity. When the field is off, those of the above electrons which succeed in getting far enough without collisions will strike the plane on the area indicated by MT, but when the field is on they will be bent round. They will travel along paths contained within the dotted lines OD and OE, and those which get far enough will strike the plane on the area represented by DE.

In the notation of fig. 1 this area amounts to  $\frac{R^2 \sin \psi}{\cos \psi} d\phi d\psi$ .

The flow per square centimetre through MP due to the group in question is

$$(\Delta n)_1 = \frac{nv \sin \theta \cos \psi d\theta}{4\pi R^2 \lambda \sin \psi d\psi} \cdot \epsilon^{-R/\lambda} d\omega. \quad (3)$$

Now the equations of motion of the electron are

$$x = vt \cos \theta + \frac{Xe}{2m} t^2, \quad (4)$$

$$y = vt \sin \theta, \quad (5)$$

where  $t$  is the time taken to go from O to E.

Now

$$\cos \psi = \frac{x}{(x^2 + y^2)^{\frac{1}{2}}}. \quad (6)$$

Substituting from (4) and (5) in (6) and neglecting second order terms (*i. e.* terms of the order  $\left(\frac{Xex}{mv^2}\right)^2$ ), and remembering that in terms multiplied by  $\frac{Xe}{mv^2}$ ,  $vt$  may be replaced by  $x/\cos \theta$ , and that in such terms  $\theta$  may be substituted for  $\psi$ , we readily obtain (see Appendix, problem 1) the result

$$\cos \psi = \left\{ 1 + \frac{Xex}{2mv^2} \tan^2 \theta \right\} \cos \theta. \quad (7)$$

On differentiating, we readily find

$$\sin \psi d\psi = \left\{ 1 - \frac{Xex}{mv^2} (1 + \frac{1}{2} \tan^2 \theta) \right\} \sin \theta d\theta. \quad (8)$$

Hence, since  $\theta$  may be replaced by  $\psi$  in terms multiplying  $Xe/mv^2$  (3) becomes

$$(\Delta n)_1 = \frac{nv}{4\pi R^2 \lambda} \left\{ 1 + \frac{Xex}{mv^2} (1 + \frac{1}{2} \tan^2 \psi) \right\} \cos \psi \cdot \epsilon^{-R/\lambda} d\omega. \quad (9)$$

It will now be convenient to take E as the origin.  $\psi$  becomes the angle made by the radius vector to the point O with the normal to MP, and the total number of electrons  $\delta n$  reaching E per square centimetre per second from the ring of volume  $2\pi R^2 \sin \psi d\psi dR$  passing through O and parallel to the plane PM is

$$\delta n = \frac{nv}{2\lambda} \left\{ 1 + \frac{Xex}{mv^2} (1 + \frac{1}{2} \tan^2 \psi) \right\} \sin \psi \cos \psi \epsilon^{-R/\lambda} d\psi dR. \quad (10)$$

\* In the expression  $\epsilon^{-R/\lambda}$ ,  $R$  should, strictly speaking, be replaced by the length of the dotted line OE, but it is easy to see that the correction on this account is a second order quantity.

To obtain the current density across the plane PM due to the electrons coming from the left of the plane, we must multiply  $\delta n$  by  $e$ , and after replacing  $x$  by  $R \cos \psi$ , integrate first with respect to  $R$  from 0 to  $\infty$ , and then from  $\psi=0$  to  $\psi=\pi/2$ . Doing this we obtain

$$\frac{nve}{2} \left\{ \frac{1}{2} + \frac{2Xe\lambda}{3mv^2} \right\} \dots \dots \dots (11)$$

The corresponding quantity due to the flow of electrons from right to left is obtained by replacing  $X$  by  $-X$  in the above, and the difference of these two current densities represents the resultant current density. Taking this difference and dividing by  $X$  we obtain for the conductivity  $\sigma$

$$\sigma = \frac{2}{3} \frac{ne^2\lambda v}{mv^2} = \frac{ne^2\lambda v}{3\alpha\theta}^*.$$

It will perhaps now be well to indicate the exact reason for the discrepancy between this result and the result indicated by equation (1) and found by Drude. In the deduction of (1) the argument usually given is equivalent to the following: "The electrons may be looked upon as all travelling the distance  $\lambda$  between two collisions, the time taken to travel this distance being  $\lambda/v$ . The velocity created by the field in this time is  $\frac{Xe\lambda}{mv}$ , and the average velocity created by the field in all the electrons to be found at an instant in any place is  $\frac{Xe\lambda}{2mv}$ . The current density is consequently  $ne \cdot \frac{Xe\lambda}{2mv}$ , which gives  $\sigma = \frac{ne^2\lambda v}{4\alpha\theta}$ ."

The portions in inverted commas must not be looked upon as the arguments of the present author. They simply represent the arguments from which (1) may be considered to have been deduced. It will be noticed that the assumption that the average velocity is half  $\frac{Xe\lambda}{mv}$  is equivalent to the assumption that the electrons to be found at any point have on the average travelled a distance  $\lambda/2$ , which appears at

\* We are not altogether justified in writing  $mv^2=2\alpha\theta$ , since the existence of a steady temperature involves that all the electrons shall not have the same velocity. The same assumption is, however, involved in (1). It is not this assumption with which I am here particularly concerned, though in Part II. of this paper I have worked out the problem taking account of the velocity distribution.



first sight true on the line of argument that the electrons are on the average in the middle of their journey  $\lambda$ . The assumption is, however, as we shall see, not true, and is one of the causes of discrepancy between (1) and (2).

Now returning to (10) and omitting the factor  $e^{-R/\lambda}$ , we have, for the number  $(\delta n)_1$  of electrons which have suffered collisions in the element specified by  $dR$  and  $d\psi$ , and which would pass through 1 square centimetre per second at E if they had suffered no more collisions,

$$(\delta n)_1 = \frac{nv}{2\lambda} \left\{ 1 + \frac{Xex}{mv^2} (1 + \frac{1}{2} \tan^2 \psi) \right\} \sin \psi \cos \psi d\psi dR. \quad (12)$$

The number  $(\delta n)_2$  of the above set to be found in 1 c.c. at E is obtained by dividing this by  $\dot{x}$ , the velocity (parallel to the  $x$  axis) which the electrons of the above set attain by the time they get to E. In the Appendix, problem (2), it is shown that

$$\dot{x} = v \left\{ 1 + \frac{Xex}{mv^2} + \frac{Xex}{2mv^2} \tan^2 \psi \right\} \cos \psi,$$

so that

$$(\delta n)_2 = \frac{n}{2\lambda} \sin \psi \cdot dR d\psi.$$

Now the number of the above set which travel a distance between  $r$  and  $r + dr$  is

$$\frac{n}{2\lambda^2} e^{-r/\lambda} dr \cdot dR \sin \psi d\psi. \quad . \quad . \quad . \quad (13)$$

From the whole range 0 to  $\pi/2$  the number is

$$\frac{n}{2\lambda^2} e^{-r/\lambda} dr \cdot dR \int_0^{\pi/2} \sin \psi d\psi = \frac{n}{2\lambda^2} e^{-r/\lambda} dr \cdot dR;$$

and taking account of the electrons which have come from the right-hand side of the plane, we have to multiply by 2, so that we have for the total number  $(\delta n)_3$  of electrons to be found per c.c. at E which have come from the shell of thickness  $dR$ , and which are in the process of travelling distances between  $r$  and  $r + dr$ ,

$$(\delta n)_3 = \frac{n}{\lambda^2} e^{-r/\lambda} dr dR. \quad . \quad . \quad . \quad (14)$$

Now keeping our attention on the electrons which travel

distances between  $r$  and  $r + dr$ , the value of  $\Sigma R(\delta n)_3$  for this set is

$$\frac{n}{\lambda^2} \epsilon^{-r/\lambda} dr \int_0^r R dR = \frac{n}{\lambda^2} \epsilon^{-r/\lambda} \frac{r^2}{2} dr; \dots (15)$$

and if  $l$  is the average distance which all the electrons to be found at E have travelled

$$nl = \int_0^\infty \frac{n}{\lambda^2} \epsilon^{-r/\lambda} \frac{r^2}{2} dr = n\lambda; \dots (16)$$

so that

$$l = \lambda.$$

We may notice that if all the electrons had travelled one and only one distance  $\lambda$  the right-hand sides of equations (15) and (16) would have both been modified to the same expression, viz.  $\frac{n}{\lambda} \cdot \frac{\lambda^2}{2}$ , so that  $l$  would have been equal to  $\lambda/2$ , which is the assumption made in the deduction of (1). In fact, though  $\lambda$  is the mean free path, we must not say that the average distance which the electrons at E have travelled is  $\lambda/2$ . It is really  $\lambda$ . If neglect of this consideration were the only error in the usual calculation of (1), the true result would be  $\sigma = \frac{ne^2\lambda v}{2\alpha\theta}$ ; but there is another source of error to which I will now refer.

It is legitimate to argue that since  $\lambda$  is the average distance which all the electrons to be found at E have travelled, the average velocity created by the field is  $\frac{Xe\lambda}{mv}$  (which is the argument made in the deduction of (1) after allowance has been made for the fact that the  $\lambda/2$  of that argument should be replaced by  $\lambda$ ), but it is not legitimate to say that the resultant current is therefore  $\frac{Xe\lambda}{mv} \cdot ne$ , the point being that the field has, as it were, sorted out the electrons differently from the two sides of the plane PM. In fact, if each of the electrons at present at E were suddenly robbed of the velocity which the field has given it, there would still be a resultant current there. We can readily see this; for on glancing at fig. 1 we remember that the electrons which have come from O to E have been bent in their path on the way. They originally started out at an inclination  $\theta$  to the normal, i. e. at a greater inclination than the angle  $\psi$ . On the other hand, the electrons which have come from the element at Q

symmetrically situated on the other side of the plane PM have been bent the other way, they originally started out at a smaller angle to the normal than the angle  $\psi$ ; so that, quite apart from the momentum communicated by the field, there was originally more momentum in the direction from right to left in the set of electrons which are to be found at E and which have come from the right of PM than there was originally momentum in the direction from left to right in the set of electrons which are to be found at E, and which have come from the left of PM. The two sets of electrons coming from elements situated symmetrically on the two sides of the plane PM are not corresponding sets, in view of the fact that their initial velocities are in different directions. Thus, it becomes necessary to add to the current density  $\frac{ne^2\lambda X}{mv}$  deduced above, the current density due to this cause,

which we will now proceed to calculate.

Omitting for the moment the part of the current directly due to the velocity communicated by the field, the electrons specified by (13) constitute a current  $\delta i_1$  such that

$$\delta i_1 = ev(\delta n)_2 \cos \theta = \frac{nev}{2\lambda^2} \epsilon^{-r/\lambda} \cos \theta \sin \psi dR dr;$$

so that using (7) and replacing  $\theta$  by  $\psi$  in the term multiplied by  $\frac{Xex}{mv^2}$ , we have

$$\delta i_1 = \frac{nev}{2\lambda^2} \epsilon^{-r/\lambda} \left\{ 1 - \frac{Xex}{2mv^2} \tan^2 \psi \right\} \cos \psi \sin \psi dR dr. \quad (17)$$

We must now put  $x = R \cos \psi$ , then integrate with respect to R from R=0 to R=r, and then from  $r=0$  to  $r=\infty$ , finally integrating with respect to  $\psi$  from  $\psi=0$  to  $\psi=\frac{\pi}{2}$ . The result is

$$i_1 = \frac{nev}{2} \left\{ \frac{1}{2} - \frac{Xe\lambda}{3mv^2} \right\} \dots \dots \dots (18)$$

The corresponding quantity due to the flow from the right-hand side of PM is obtained by replacing X by  $-X$  in (18), and the current resulting from  $i_1$  and  $i_2$  is thus

$$i_1 - i_2 = -\frac{ne^2\lambda v X}{3mv^2}.$$

The total resultant current density is thus

$$\frac{ne^2\lambda X}{mv} + i_1 - i_2 = \frac{2}{3} \frac{ne^2\lambda v X}{mv^2} = \frac{ne^2\lambda v X}{3\alpha\theta}^*.$$

Giving for the conductivity  $\sigma$ ,

$$\sigma = \frac{ne^2\lambda v}{3\alpha\theta},$$

which is the result found on pages 441-445.

PART II.—*Calculation of the electrical conductivity for the case where the velocities of the electrons are distributed according to Maxwell's law in the absence of the electric field, and where the number of electrons starting out in any infinitesimal velocity range, from an element in which they have suffered collisions, is the same when the field is present as when it is absent.*

The number of electrons per c.c. having velocities between  $c$  and  $c + dc$  is, in the absence of the field,

$$Ae^{-hm c^2} c^2 dc,$$

where

$$A = \frac{4n}{\sqrt{\pi}} (hm)^{3/2}, \quad \text{and} \quad hm = \frac{3m}{4\alpha\theta}.$$

If in (11) we replace  $v$  by  $c$ ,  $n$  by  $Ae^{-hm c^2} c^2 dc$ , the resulting expression will be the current density  $\delta j_1$  due to the flow from left to right of that group of electrons which have velocities between  $c$  and  $c + dc$ . The result is

$$\delta j_1 = \frac{A}{2} e^{-hm c^2} c^3 \left\{ \frac{1}{2} + \frac{2Xe\lambda}{3mc^2} \right\} dc.$$

The corresponding current density  $\delta j_2$  due to the flow from right to left is obtained by replacing  $X$  by  $-X$  in the above, and the resultant current due to all the electrons whose

\* It is to be noted that the part  $\frac{ne^2\lambda X}{mv}$ , i. e.  $\frac{ne^2\lambda v}{2\alpha\theta}$ , represents the only part of the current accounted for by Drude. The fact that he obtained  $\frac{ne^2\lambda v}{4\alpha\theta}$  is simply due to the improper use of the quantity  $\lambda$  already referred to.

It is interesting to notice that if we were to imagine that all the electrons for some reason or other travelled one and only one distance  $\lambda$ , we should have  $\sigma = \frac{2}{3} \frac{ne^2\lambda v}{\alpha\theta}$ .



velocities lie between  $c$  and  $c+dc$  is  $\delta j_1 - \delta j_2$ . Writing  $\delta j$  for this we have

$$\delta j = \frac{2AXe^2\lambda}{3m} \epsilon^{-hmc^2} c \, dc;$$

$$\therefore j = \frac{2AXe^2\lambda}{3m} \int_0^\infty \epsilon^{-hmc^2} c \, dc. \quad . \quad . \quad (19)$$

On replacing  $A$  and  $hm$  by the values given above and writing  $u$  for the square root of the mean square velocity, we obtain

$$\sigma = \sqrt{\frac{2}{3\pi}} \cdot \frac{ne^2\lambda u}{\alpha\theta}, \quad . \quad . \quad . \quad (20)$$

which happens to be the same result as that obtained by Lorentz by a different method.

### *The Thermal Conductivity.*

The determination of the thermal conductivity for a gas when the molecules obey Maxwell's law is a well-known problem. We shall, however, briefly survey the steps for the purpose of applying it to the present problem.

If in (10) we put  $X=0$ , and replace  $n$  by  $A\epsilon^{-hmc^2} c^2 \, dc$ ,  $v$  by  $c$ , and  $\lambda$  by  $\lambda_c$  where  $\lambda_c$  is the free path for velocity  $c$ , and where the values refer to the plane PM, we shall obtain the number of electrons which reach E per square centimetre per second, which have come from the ring of volume  $2\pi R^2 \sin \psi \, d\psi \, dR$ , and whose velocities are contained within the limits  $c$  and  $c+dc$ .

We have for the number

$$\frac{A}{2\lambda_c} \epsilon^{-hmc^2} c^3 \, dc \cdot \epsilon^{-R/\lambda_c} dR \sin \psi \cos \psi \, d\psi.$$

Remembering that  $\alpha\theta$  is the mean kinetic energy of an electron at a temperature  $\theta$ , we have for the transference of energy  $Q_1$  per square centimetre per second across the plane PM at E, the result

$$Q_1 = \frac{A}{2} \int_0^\infty \frac{\epsilon^{-hmc^2}}{\lambda_c} c^3 \, dc \int_0^{\pi/2} \sin \psi \cos \psi \, d\psi \int_0^\infty \epsilon^{-R/\lambda_c} \left\{ \alpha\theta - \alpha \frac{d\theta}{dx} \cdot R \cos \psi \right\} dR.$$

The corresponding quantity representing the flow from right to left is obtained by replacing  $\frac{d\theta}{dx}$  by  $-\frac{d\theta}{dx}$ , and the resultant thermal current density is obtained by subtracting

these two quantities. The conductivity  $k$  is obtained by dividing this by  $\frac{d\theta}{dx}$ . We thus have

$$k = \frac{A\alpha}{3} \int_0^\infty \epsilon^{-hm c^2} c^3 \lambda_c dc = \frac{4n\alpha}{3\sqrt{\pi}} (hm)^{\frac{3}{2}} \int_0^\infty \epsilon^{-hm c^2} c^3 \lambda_c dc. \quad (21)$$

For the present case, where we take  $\lambda_c$  as constant, we find

$$k = \frac{2}{3} \sqrt{\frac{2}{3\pi}} n \lambda u \alpha,$$

and using (20)

$$\frac{k}{\sigma} = \frac{2\alpha^2\theta}{3e^2} = 3.6 \times 10^{10} \text{ at } 0^\circ \text{ C.,}$$

which is very far from the experimental value.

If the mean free path were a function of the velocity, as might conceivably happen if the centres inside the atoms with which the collisions occur were in motion, the expressions for  $k$  and  $\sigma$  would require modification.  $\lambda_c$  would have to be retained inside the integral in equation (21), and if  $\lambda_c$  were a function only of the initial velocity with which the electron started out after collision, the only modification which would be necessary in the calculation of  $\sigma$  would be to retain  $\lambda_c$  inside the integral in (19), so that we should have

$$\frac{k}{\sigma} = \frac{\alpha m}{2e^2} \frac{\int_0^\infty \epsilon^{-hm c^2} c^3 \lambda_c dc}{\int_0^\infty \epsilon^{-hm c^2} c \lambda_c dc}.$$

If, for example,  $\lambda_c$  were proportional to  $c^n$ , we should have

$$\frac{k}{\sigma} = \frac{\alpha}{2e^2 h} \cdot \frac{\Gamma\left(\frac{n}{2} + 2\right)}{\Gamma\left(\frac{n}{2} + 1\right)} = \frac{2\alpha^2\theta}{3e^2} \left(\frac{n}{2} + 1\right),$$

so that if  $\lambda_c$  were proportional to  $c^{\frac{5}{2}}$ , we should have

$$\frac{k}{\sigma} = 6.3 \times 10^{10},$$

which is just the correct value.

Unfortunately, when we form a physical picture of the phenomenon it does not seem reasonable to try in the problem

of electrical conduction to take full cognizance of the essential phenomena by expressing the mean free path as a function of the velocity with which the electron started its journey, since we should expect that the factor which would determine whether an electron suffered a collision in any given element would be its velocity while *in* that element, and this would depend upon the distance which the electron had travelled resolved parallel to the field as well as upon its initial velocity. In fact, it is probably more reasonable to state the case in the following way.

Let  $\lambda_c$  be the mean free path for a velocity  $c$  in the absence of the field, and let the fraction of  $N$  electrons which suffer collisions in passing through an element of thickness  $d\zeta$  be  $f(\zeta)d\zeta$ , so that

$$-\frac{dN}{d\zeta} = Nf(\zeta) \quad \text{and} \quad N = N_0 e^{-\int_0^\zeta f(\zeta) d\zeta}.$$

When  $\zeta$  is a constant over the path of an electron and equal to the velocity  $c$  with which the electron started out, the integral becomes  $\zeta f(c)$ , which shows that  $f(c) = 1/\lambda_c$ . In order to obtain the number of electrons  $\delta n'$  coming out from the ring of volume  $2\pi R^2 \sin \psi d\psi dR$  (p. 444) and passing through  $E$  per square centimetre per second, and whose velocities lie between  $c$  and  $c + dc$ , it is necessary to replace  $\frac{nv}{2\lambda}$  in equation (10) by  $\frac{A\epsilon^{-\frac{1}{2}mc^2} c^2 dc}{2\lambda_c}$ \*,  $v$  by  $c$ , and  $\epsilon^{-R/\lambda}$  by

$$\epsilon^{-\int_0^R f\left(c^2 + \frac{2Xex}{m}\right)^{\frac{1}{2}} dR},$$

since if  $c$  is the velocity with which an electron starts out, its velocity after travelling a distance whose component parallel to the field is  $x$  amounts to  $\left(c^2 + \frac{2Xex}{m}\right)^{\frac{1}{2}}$ .

Now if we expand  $f\left(c^2 + \frac{2Xex}{m}\right)^{\frac{1}{2}}$  by Taylor's theorem,

then integrate with respect to  $R$  remembering that  $x = R \cos \psi$ , and finally replace  $f(c)$  by  $1/\lambda_c$ , we readily find

$$\epsilon^{-\int_0^R f\left(c^2 + \frac{2Xex}{m}\right)^{\frac{1}{2}} dR} = \epsilon^{-R/\lambda_c} \epsilon^{\frac{R^2 X e \cos \psi}{2m\lambda_c^2 c} \cdot \frac{\partial \lambda_c}{\partial c}} = \left\{ 1 + \frac{R^2 X e \cos \psi}{2m\lambda_c^2 c} \cdot \frac{\partial \lambda_c}{\partial c} \right\} \epsilon^{-R/\lambda_c}.$$

\* It will be noticed that the total number of electrons starting out from an element after suffering collisions therein cannot be affected by the field to the first power of  $\frac{Xe}{mc^2}$ .

Thus

$$\delta n' = \frac{A\epsilon^{-\hbar m c^2}}{2\lambda_c} c^3 dc \left\{ 1 + \frac{Xex}{mc^2} \left( 1 + \frac{1}{2} \tan^2 \psi + \frac{Rc}{2\lambda_c^2} \cdot \frac{\partial \lambda_c}{\partial c} \right) \right\} \epsilon^{-R/\lambda_c} \sin \psi \cos \psi d\psi dR.$$

The remainder of the work is now exactly analogous to that carried out on pages 445 and 449, and we obtain

$$\sigma = \frac{2}{3} \frac{Ae^2}{m} \left\{ \int_0^\infty \epsilon^{-\hbar m c^2} \lambda_c c^2 dc + \frac{1}{2} \int_0^\infty \epsilon^{-\hbar m c^2} \frac{\partial \lambda_c}{\partial c} \cdot c^2 dc \right\}.$$

Integrating the second term by parts we finally obtain

$$\sigma = \frac{2}{3} Ae^2 h \int_0^\infty \epsilon^{-\hbar m c^2} \lambda c^3 dc.$$

Thus, using (21) we have

$$\frac{k}{\sigma} = \frac{2}{3} \frac{\alpha^2 \theta}{c^2}.$$

The result is thus independent of the manner in which  $\lambda_c$  varies with the velocity.

#### APPENDIX.

*Problem (1).*

To show that  $\cos \psi = \left\{ 1 + \frac{Xex}{2mv^2} \tan^2 \theta \right\} \cos \theta$ .

Substituting in (6) from (4) and (5) we have, neglecting second-order quantities,

$$\begin{aligned} \cos \psi &= \frac{\left( v \cos \theta + \frac{Xe}{2m} t \right) t}{\left\{ v^2 t^2 \cos^2 \theta + \frac{Xev}{m} t^3 \cos \theta + v^2 t^2 \sin^2 \theta \right\}^{\frac{1}{2}}} \\ &= \left( 1 + \frac{Xet}{2mv \cos \theta} \right) \left( 1 + \frac{Xet \cos \theta}{mv} \right)^{-\frac{1}{2}} \cos \theta. \end{aligned}$$

Putting  $vt \cos \theta = x$ , we readily obtain

$$\cos \psi = \left\{ 1 + \frac{Xex}{2mv^2} \tan^2 \theta \right\} \cos \theta.$$



*Problem (2).*

To show that  $\dot{x} = v \left\{ 1 + \frac{Xex}{mv^2} + \frac{Xex}{2mv^2} \tan^2 \psi \right\} \cos \psi$ .

From (4) we have

$$\dot{x} = v \cos \theta + \frac{Xe}{m} t = \left\{ 1 + \frac{Xex}{mv^2 \cos^2 \theta} \right\} v \cos \theta.$$

Replacing  $\cos \theta$  by its value in terms of  $\cos \psi$  as found from Problem (1), we have

$$\begin{aligned} \dot{x} &= \left\{ 1 + \frac{Xex}{mv^2 \cos^2 \theta} - \frac{Xex}{2mv^2} \tan^2 \theta \right\} v \cos \psi \\ &= \left\{ 1 + \frac{Xex}{mv^2} + \frac{Xex}{2mv^2} \tan^2 \psi \right\} v \cos \psi. \end{aligned}$$

The University of Sheffield.  
July 30th, 1913.

*Note added Dec. 26th, 1913.*

Since the above paper was written, certain further matters in relation to the history of expressions (1) and (2) have come to my notice.

Before Drude published the expression (1), and as early as 1898, E. Riecke (*Wied. Ann.* Bd. lxvi. pp. 353 *et seq.*, 1898), in a paper in which both positive and negative carriers were included, obtained an expression which when interpreted in terms of the modern electron theory would amount to

$\sigma = \frac{ne^2 \lambda v}{2\alpha \theta}$ . In the same year, and still before the publi-

cation of Drude's paper, Riecke found it necessary to introduce a correction into his calculation which actually

results in the expression  $\sigma = \frac{ne^2 \lambda v}{3\alpha \theta}$  deduced above (see *Wied.*

*Ann.* Bd. lxvi. p. 1199, 1898). In spite of this fact, Drude's

result  $\sigma = \frac{ne^2 \lambda v}{4\alpha \theta}$  is still quoted in all the well known books

dealing with the subject; and this fact is the more remarkable since the difference between the two formulæ is not the outcome of any difference in the fundamental assumptions in the two methods, but is simply due to an error in Drude's work, which, as is shown in the present paper, is of a purely mathematical nature.

While this paper was in the press, I learned from Dr. Niels Bohr, during conversation, that he has referred to the discrepancy between the two expressions in a footnote on page 54 of his 'Dissertation' (which is printed in Danish), and has remarked that it is due to the erroneous method by which Drude calculated the mean velocity communicated to the electrons by the field. In spite of these facts, the parts of the present paper dealing with this matter will I think be found of interest in indicating more precisely the exact point, or rather points (for there are two) which are involved in the rather subtle explanation of the discrepancy.

**XLIX. On Nuclear Electrons. By A. VAN DEN BROEK \*.**

**T**HAT the intra-atomic charge is equal not to half the atomic weight, but to the number  $M$  each element occupies in Mendeleejeff's series arranged in order of increasing atomic weight, follows from the ratio of the scattering of  $\alpha$ -particles per atom divided by the square of that number being a real constant ( $18.7 \pm 0.3$  for Cu, Ag, Sn, Pt, Au), as according to Rutherford must be the case for that ratio divided by the square of the charge, while if the square of half the atomic weight is taken, these numbers show systematic diminution from, if as mean value  $18.7$  too is taken,  $20.6$  for Cu to  $17.5$  for Au †.

TABLE I.

	Cu.	Ag.	Sn.	Pt.	Au.	Mean.
Scattering $\div \frac{A^2}{5.4}$ ...	20.6	18.9	18.1	17.8	17.5	18.6
$M$ .....	29	47	50	82	83	
Scattering $\div M^2$ .....	18.5	18.4	19.0	18.6	18.4	18.6

As these nuclear charges for U and Pb, as for Th and Bi, give other differences than the number of positive charges lost by expulsion of the  $\alpha$ -particles (the nuclear charge difference being 10 for U and Pb, and 7 for Th and Bi,

\* Communicated by the Author.

† Geiger & Marsden, Phil. Mag. xxv. p. 604 (1913).

while the number of positive charges expelled are 16 and 12 resp.), no other explanation seems possible than that  $\beta$ -particles—6 for the U-series and 5 for the Th-series—are ejected too from the nucleus\*.

Indeed, the number of  $\beta$ -ray products in these two series corresponds (complex radiation being taken into account) completely with these numbers.

The same conclusion may be arrived at on quite another line. The periodic number  $P$  an element occupies in a strictly periodic series from Li upwards with each triad of group VIII, and all the elements from Ce to Ta concentrated into one place each, can be proved to be equal to  $\sqrt{\frac{A-2M}{2c}}$  ( $M$  being the number in Mendeleeff's series,  $A$  the atomic weight, and  $c$  a constant).

Thus, if the total number of electrons per atom is equal (as from the mass and charge of the  $\alpha$ -particle may be supposed,  $4/5$  of all known atomic weights being of the types  $4n$  and  $4n+3$ ) to half the atomic weight, we get

$$N - M = cP^2,$$

and as  $M$  is equal too to the number of electrons surrounding the nucleus,  $cP^2$  must be the number of electrons in the nucleus.

Here again we find for U and Pb, as for Th and Bi, the same differences, 6 and 5 resp., as must be expected from the number of  $\beta$ -rays expelled.

TABLE II.

	C.	Mg.	Ar.	Cr.	Zn.	Kr.	Mo.	Cd.	Xe.	Nd.	W.	Pb.	Bi.	Th.	U.
M ...	6	12	18	24	30	36	42	48	54	60	78	86	87	94	96
P .....	4	10	16	22	26	32	38	42	48	52	54	60	61	68	70
$cP^2$ ...	0	0	1	2	3	5	6	8	11	12	14	17	17	22	23
$A_{\text{calc.}}$	12	24	38	52	66	82	98	112	130	144	184	206	208	232	238
$A_{\text{exp.}}$	12	24	40	52	65	82	96	112	130	144	184	207	208	232	238

$$A_{\text{calc.}} = 2(M + cP^2); c = 0.00468.$$

The number of nuclear electrons being proportional to the periodic number  $P$ , and this number remaining unchanged

\* Compare Bohr, Phil. Mag. xxvi. p. 500 (1913).

from Ce to Ta, all these rare earths must contain the same number of nuclear electrons.

Should the  $\alpha$ -particle be composed of  $4(H^+) + 2$  electrons, then the number of nuclear electrons should be for U 142, that of the positive units 238, and, 380 particles occupying about  $2.7 \times 10^{-25}$  c.cm.\*; the positive unit must be of equal size, if not identical with the electron ( $0.5 \times 10^{-37}$ ), but in a different state.

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*L. Note on the Electron Atmosphere (?) of Metals.*

*By* CARL R. ENGLUND †.

IN an article published last year ‡ Professor R. W. Wood has advanced a theory of an electron atmosphere to account for some results which he obtained. Some experiments performed by me, at Professor Millikan's suggestion, in the Ryerson Laboratory in the University of Chicago, in the spring of 1911, on sparking potentials at small distances, gave results which appear irreconcilable with such a theory and it is perhaps worth while to mention them here.

A spark-gap was mounted on an interferometer; one of the electrodes was carefully insulated with ebonite, and both electrodes were provided with mirrors so as to form a double-fringe system. This eliminated the possibility of a deformation in the supports which might render the sparking distance between the electrodes at the instant of discharge something less than the distance read upon the double interferometer system. The insulated electrode was connected to a Wilson electroscope, the capacity of the electroscope and electrode being only a few centimetres, and the other electrode was connected to one terminal of a storage-battery giving up to 500 volts. The other battery terminal and electroscope-case were of course earthed (see figure for the connexions). By this means the quantity of electricity discharged during a spark was reduced to the smallest possible amount and a minimum corrosion of the electrodes was obtained.

Measurements of the sparking potentials between silver, nickel, and soft steel electrodes, one plane and the other having a radius of 1 cm., *from one half to four sodium wavelengths apart*, gave substantial verification of Hobbs's § earlier

\* Rutherford, 'Radioactive Substances,' 1913, p. 621.

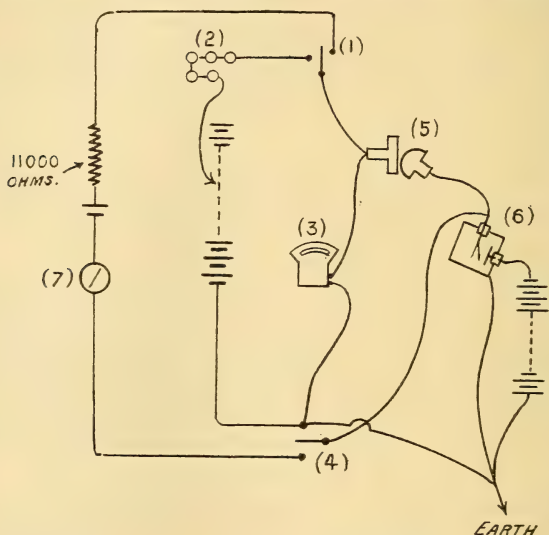
† Communicated by Prof. R. A. Millikan.

‡ R. W. Wood, *Phil. Mag.* [6] xxiv. p. 316 (1912).

§ Hobbs, *Phil. Mag.* [6] ix. p. 617 (1905).



results. The air-film in every case remained an insulator until the voltage reached the sparking potential, when a charge passed over to the electroscope. This operation was usually



- |                             |                          |
|-----------------------------|--------------------------|
| (1) Switch.                 | (5) Spark-gap.           |
| (2) Lamp res. of 4400 ohms. | (6) Wilson electroscope. |
| (3) Static voltmeter.       | (7) Galvanometer.        |
| (4) Switch.                 |                          |

instantaneous, although occasionally a gradual leak through the insulation seemed to take place. Dust particles or a water-film could in such cases be instantly detected, and hence the electrodes were always carefully cleaned and gently heated before using. If consistent sparking potentials with accompanying insulation between the electrodes down to distances of one-half of a sodium wave-length can thus be obtained, it would seem that the hypothesis of an "Electron Atmosphere" is untenable. At this distance the voltage necessary for discharge was between 80 and 100 volts, and no more delicate test than the electroscope deflexion could well be demanded of an insulator. Wood's "Electron Atmosphere" seemed to extend to a distance of as much as 30 wave-lengths. A recent paper by Brown\* seems to indicate that a film of moisture constitutes the "Electron Atmosphere."

Ann Arbor, Mich.  
Nov. 8, 1913.

\* Brown, Phys. Rev. Oct. 1913.

LI. *The Decline of the Hypothesis of Ionic Dissociation.*  
 By F. P. WORLEY, D.Sc. (London), Professor of Chemistry,  
 Auckland, New Zealand\*.

**D**URING the past quarter of a century the doctrine of ionic dissociation, formulated by Arrhenius in 1883-87, has been so persistently advocated that few chemists now regard it as a mere hypothesis; the majority fail to see that no single convincing argument necessitating the hypothesis has ever been brought forward and that its acceptance has been due to the plausibility of the arguments by which, apparently, it may be supported rather than to their cogency: nor is it recognized how far from being secure are not only the minor supports on which it rests but also some, if not all, of those upon which most reliance is placed.

The very simple explanation the hypothesis apparently afforded of so many chemical phenomena left little doubt in the minds of its early advocates that further investigation would dispose of difficulties such as are presented by concentrated solutions and strong electrolytes, for example; but although, of late years, a good deal of fresh evidence has been adduced which has appeared to support the doctrine, difficulties such as those referred to have not been removed†; indeed, it is now tacitly admitted that such phenomena as the colour of salt solutions and the mutual precipitation of salts can no longer be cited in support of the hypothesis. Moreover, much has been done to show that the explanation of the catalytic effect exercised by acids—in the case of changes such as those attending the hydrolysis of cane-sugar and of ethereal salts and the reverse change of etherification—by the hypothesis presents very formidable difficulties and that the effect can be accounted for rationally without its aid‡; especially difficult of explanation is the part played by neutral salts in such phenomena.

One of the strongest arguments put forward by Arrhenius in favour of his hypothesis was the fact that it was possible to correlate the chemical activity of electrolytes with the presumed degree of ionic dissociation as deduced from their molecular electrical conductivities: hence the dissociated ions alone of electrolytes were postulated as concerned in

\* Communicated by Dr. H. E. Armstrong, F.R.S.

† Arrhenius, 'Theories of Solutions,' p. 172.

‡ Roy. Soc. Proc. A. lxxxvii. p. 604 (1912). "Studies of the Processes Operative in Solutions. XXIV. The Nature of the Hydrolytic Process." By H. E. Armstrong and F. P. Worley.

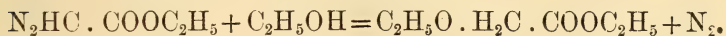
conveying the current and these ions also were supposed to be the sole cause of chemical interactions. According to this view, *dissociation* is the immediate antecedent of every chemical interchange, an interpretation which is in opposition to the view, first definitely expressed by Kekulé and since advocated by a small school of chemists, notably by Armstrong in England and Michael in America, that *association* of the molecules concerned is the necessary antecedent. The activity of acids has always been attributed by Arrhenius and his followers to their hydrogen ions and a great deal of work has been done with the object of showing the close connexion between such chemical activity and the presumed concentration of the hydrogen ions deduced from measurements of electrolytic conductivity. Ostwald's early research on the subject showed that the hydrolytic activity of acids was in the order of the degree of assumed ionic dissociation; and a vast amount of investigation has since been carried out with the object of showing that the one is exactly proportional to the other. This object has not been realized and very serious discrepancies have been shown to exist which the supporters of the Arrhenius hypothesis have failed to explain and have frequently been very loath to recognise. One is the influence above referred to which neutral salts exercise upon hydrolytic phenomena. The hydrolytic activity of any strong acid is considerably increased by the addition of a neutral salt of the acid: for instance, when cane-sugar is hydrolysed by an aqueous solution of hydrogen chloride, the rate of hydrolysis is very much increased by the addition of sodium chloride and still more by calcium chloride. The effect produced is entirely opposite to that demanded by the dissociation hypothesis, as instead of increasing the concentration of the hydrogen ions the salt should, in fact, diminish it. This "neutral salt action" has received considerable attention, especially from Arrhenius himself; but it has not been satisfactorily explained on the basis of his hypothesis.

Another difficulty is the fact that the molecular hydrolytic activity of an acid, at least of a strong acid, decreases as dilution is increased, instead of increasing as it should if its activity were proportional to the degree of ionic dissociation. The acid itself appears to have a "neutral salt action." This difficulty, which is perhaps the most formidable of all, has been constantly avoided and, as will be shown later, has apparently been entirely overlooked by some of the chief workers on this branch of the subject.



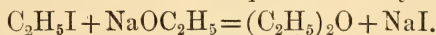
An important change of front has been made independently, in the same direction, by Bredig and Snethlage\* in Germany and by Acree† and his co-workers‡ in America. These ardent supporters of the Arrhenius hypothesis have come to the remarkable conclusion that an electrolyte in solution may enter into chemical interactions both by means of its ions and also by means of its undissociated molecules—that the catalytic action of acids, for instance, is due both to the hydrogen ions and to the undissociated molecules. Such a conclusion is of vital importance but it cannot fail to breed confusion in the ionic camp, as it involves the sacrifice of the very important connexion between electrical and chemical phenomena which has been the mainstay of the dissociation hypothesis.

Bredig and Snethlage arrived at their conclusion from an investigation of the change in the catalytic activity of an acid produced by the addition of a neutral salt of the acid. The interaction investigated was that between ethylic diazoacetate and absolute alcohol in the presence of either picric or some other weak acid as catalyst:—



Snethlage found that the hydrolytic activity could be reduced to a limiting value by adding a sufficient amount of a salt of the acid. He supposes that under these conditions the ionic dissociation of the acid is almost completely suppressed and that the observed catalytic activity is due to the non-ionized acid molecules alone. From his results he deduced the ratio of the activities of the undissociated molecules of the acids used to that of the hydrogen ion.

Acree's conclusion has been arrived at from the study of the effect of dilution on such changes as the interaction of ethyl halides and ethylates or phenolates of the alkali metals dissolved in absolute alcohol, by which change the alkaline halide and an ether are produced, *e. g.*



Constants are obtained expressing the velocity with which the interaction would proceed if the concentration of the ethylate or phenolate were reduced to unity and the degree of ionic dissociation at the different dilutions were unchanged. In other words, these constants express the molecular activity

\* *Chemiker Zeitung*, May 25, 1912, p. 687; *Zeits. Elektrochem.* xviii. p. 839 (1912).

† *Amer. Chem. Journ.* xlviii. p. 352 (1912).

‡ Robertson and Acree, *ibid.* xlix. p. 474 (1913).



of the electrolyte at different dilutions and different degrees of ionic dissociation. The velocity coefficients so calculated increase as dilution is increased but at a lower rate than the assumed degree of ionization of the electrolyte. In the experiment cited (*l. c.* p. 355) the value of the velocity coefficient, expressing the molecular activity of sodium ethylate, increases from 0.075 to 0.0998, when the dilution is changed from one molecular proportion in two litres to one in forty litres, the corresponding change in ionic dissociation being from 0.148 to 0.605. It is clear that the velocity of interaction cannot be correlated with the concentration of the assumed ethylate ion alone. The assumption has therefore been made that it is dependent both on the ethylate ions and also on the non-ionized sodium ethylate molecule. By solving a series of simultaneous equations, values of  $K_i$  and  $K_m$  are obtained expressing the activity of the ion and of the molecule respectively. In the experiment cited the values of  $K_i$  and  $K_m$  have a remarkable degree of constancy but more important is the fact that the value of  $K_i$  for the ethylate ion, arrived at from experiments with sodium ethylate and potassium ethylate, is practically the same for both salts, though the values of  $K_m$  for the molecules are different. In the case of the phenolates of lithium, sodium and potassium, the values of  $K_i$  for the phenolate ion are nearly identical, while those of  $K_m$  for the molecules vary considerably. It is impossible at present to discuss other possible explanations of this numerical agreement than the one advanced. Although Acree has for some time advanced the view that in hydrolytic change undissociated molecules may be partly concerned, he is guarded in his acceptance of the results as a proof of the truth of his hypothesis and it must always be borne in mind that there may be various possible explanations for such numerical agreement. However, it is not the object of this paper to discuss the methods by which Bredig and Snelthage and Acree have arrived at their conclusion but rather to examine some of the consequences of this remarkable change of attitude on the part of supporters of the doctrine of ionic dissociation.

In the first place, it is not necessary to confine our attention to non-aqueous solutions as the above investigators have done. Acree's method especially is very widely applicable, as the molecular chemical activity of an electrolyte rarely changes in exactly the same way on change of concentration as its degree of ionic "dissociation." This important fact has been much neglected by supporters of the ionic dissociation

hypothesis and it is encouraging to find that it is being recognized. In the case of the hydrolysis of ethereal salts and of cane-sugar, although the two properties are altered in different directions by alterations of concentration, Acree and Stieglitz, two of the chief workers on the subject of hydrolysis, evidently imagine that they run parallel, as they repeatedly state in emphatic terms that the rate of hydrolysis is proportional to the concentration of the hydrogen ions.

TABLE I.

Molecular Proportions $H_2O : HCl.$	Molecular hydrolytic activity of acid.	Degree of "ionization" $\frac{\mu}{\mu_{\infty}}$
<i>n</i>		
30	385	0.725
40	323	0.778
50	290	0.813
60	269	0.837
80	243	0.859
100	229	0.871
200	201	0.901

TABLE II.

Dilutions (Mols. $H_2O$ ).	$K_i$ .	$K_m$ .
30 : 60	100	1136
30 : 80	94	1154
30 : 100	91	1160
30 : 200	98	1143
40 : 80	104	1092
40 : 100	99	1110
40 : 200	103	1095
50 : 80	99	1121
50 : 100	92	1145
50 : 200	101	1112
60 : 100	77	1254
60 : 200	96	1159
80 : 100	79	1245
80 : 200	102	1102
100 : 200	109	1042
Mean .....	96	1138

Thus Stieglitz \* writes—

“In the case of the catalysis of the esters we are certain of three main facts which have been proved experimentally: the action is accelerated in proportion to the concentration of the hydrogen ions present .....

Acree and Johnson†, in reference to their explanation of hydrolytic change, say—

“The assumption explains ....., why the velocity of saponification and esterification increases directly in proportion to the concentration of the hydrogen ions.”

The fact, however, has long been patent that this is by no means the case. The entirely opposite effects of dilution on the molecular hydrolytic activity and the degree of presumed ionic dissociation of hydrogen chloride in aqueous solution is clearly shown in Table I. On applying Acree's method to this case, in which cane-sugar was the hydrolyte, we arrive at the conclusion (see Table II.) that the undissociated molecule of hydrogen chloride is as much as twelve times as active as the hydrogen ion. The experiments were not carried out for this purpose and the changes of concentration are not great enough to give smooth results: but there can be no doubt that on Acree's assumption the molecule is far more active when non-dissociated than when dissociated into ions.

The molecular hydrolytic activity of the stronger acids generally in aqueous solutions decreases with dilution; and if we assume that the divergence from the course followed by the degree of ionic dissociation is due to the fact that the molecules and ions are both active, we are driven to admit a degree of activity for the acid molecule greater than that of the presumed hydrogen ion.

Now it is the close connexion that exists between chemical activity, especially as exhibited by precisely the above hydrolytic activity and the degree of ionic dissociation measured electrically, that has appeared to form so strong an argument in favour of the ionic dissociation hypothesis; and, indeed, if it could be maintained, as most supporters of the hypothesis have believed to be the case, that the chemical activity of acids is proportional to the concentration measured electrolytically of the dissociated ions, presumed to be alone responsible for the acidity, there would undoubtedly be considerable support for the ionic dissociation hypothesis. The admission, however, that the hydrogen ions and the undissociated acid molecules are both active chemically undermines

\* Amer. Chem. Journ. xxxix. p. 30 (1908).

† *Ibid.* xxxviii, p. 341.

this support completely and leaves the matter, so far as the ionic dissociation hypothesis is concerned, in a state of extreme confusion. The strength of acids should not, according to the new point of view, be proportional to their hydrogen ion concentration and it will be interesting to see if ionists will turn their backs on their old friend and admit that this is the case.

The close connexion that undoubtedly exists between chemical and electrolytic activity is in all probability due to their both being manifestations of the same process: in other words, the passage of a current through a solution of an electrolyte is conditioned by chemical action and chemical action itself is an electrolytic process. Perhaps the ionists will now find a loophole of escape in the admission that ions and undissociated molecules may both be concerned in conveying an electric current but this would obviously be a suicidal step. It is highly interesting, however, that the possibility of this being the case has recently been put forward by G. N. Lewis\*.

The granting of a franchise to the non-ionized molecules, so allowing them as well as the ions to partake directly in chemical change, places a further obstacle in the path of the ionists. It will necessitate serious alteration of the beautifully simple explanation they have given of chemical action occurring in solutions of electrolytes: as, for instance, of the processes involved in qualitative analysis. Ions alone were supposed to be directly involved in the interactions and precipitation was explained as due to the combination of ions derived from different interacting molecules to form undissociated molecules of a new type, relatively insoluble in water. Nothing more was involved than dissociation into ions and recombination of the latter to form the various possible molecular species. In the case of molecules that can interact without being first dissociated, another type of action must be postulated. The ionists must, in fact, accept for the non-dissociated molecules the view of their opponents, that *association* of the interacting molecules precedes the chemical interchange of radicles. Thus, for interactions in solutions of electrolytes, we shall have to assume two diametrically opposite kinds of chemical change occurring simultaneously, one in which *dissociation* and another in which *association* of the involved molecules is the first step. The weakness of such an explanation is only too obvious.

The supporters of the ionic dissociation hypothesis are thus apparently faced with serious difficulties if they accept the

\* Journ. Amer. Chem. Soc. xxxiv. p. 1642 (1912).



conclusions arrived at by Acree and his co-workers and by Bredig and Sneath. On the other hand, if they do not accept them, the equally grave difficulties which these investigators have attempted to remove still remain unexplained on their hypothesis.

The Arrhenius hypothesis undoubtedly owes its great popularity to the remarkably simple picture it professes to give of the nature of solutions of electrolytes and the processes occurring in them. Unfortunately, the picture is a great deal too simple. Of its various shortcomings, mention may be made here of its almost complete disregard of the part played in chemical interactions by the solvent, a defect of the very greatest importance. Again, it expresses all changes in activity as being due to changes in the mere number of the active units, ignoring the possibility of alterations in the degree of activity of the active units accompanying changes in dilution. This is the more remarkable now that ionists recognize that if not hydrated, ions are at least surrounded by spheres of attached water molecules and that the amount of attached water is dependent on the dilution. The part played in chemical change by this attached water is not considered nor the fact that the condition of the water not so attached is altered by the presence of substances in solution. Water, it must be remembered, is a complex equilibrated mixture of different polymers of the simple molecule represented by the formula  $H_2O$  (hydrone) and the presence of any dissolved substance is almost certain to disturb the equilibrium.

On the other hand, the accumulated evidence in favour of chemical interaction being preceded by association of the interacting molecules is very great indeed. In the case of hydrolysis effected by the agency of enzymes, there is little doubt that the enzyme and the hydrolyte become intimately associated before hydrolysis takes place. When acids are the hydrolytic agents, the phenomena observed under the most varied conditions are apparently quite in accord with the view: that hydrolysis is effected by the association and subsequent interaction of a molecule of the hydrated catalyst with one of the hydrated hydrolyte: that the acid catalyst presents water to the hydrolyte in much the same way as does the enzyme. It is apparently only the water actually attached to the interacting molecules that enters directly into the hydrolytic change. The complexes which are formed may break down in various ways and many of the cleavages result in a return to the original components, only a fraction being effective as far as hydrolysis is concerned. Decrease

of molecular hydrolytic activity accompanying dilution of the acid is not only easily explained but appears to be demanded by this view of the mechanism of hydrolytic change and the reverse change of etherification—for, as dilution is increased the acid becomes more and more hydrated towards a maximum; or at least, more under control of the water; and the more its activity is exerted in this direction, the less will it have left for combination with a hydrolyte. The large influence which water has on the activity of acids in alcoholic solution, as shown by Goldschmidt, Lapworth and Bredig, is quite in accordance with this view and exceedingly difficult to explain on the ionic hypothesis.

In conclusion, I may urge that, in my opinion, the hydrolytic activity of acids and indeed the chemical activity of electrolytes generally does not support the hypothesis of ionic dissociation, though it most emphatically shows the close connexion between chemical and electrolytic activity, irrespective of any theory of the nature of electrolytic activation. Chemists have greatly neglected the distinction between these two issues and have advanced as evidence in favour of the Arrhenius hypothesis what really is evidence only of the close connexion between electrolytic activity and chemical activity. This is especially true of hydrolytic phenomena.

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LII. *A Note on Prof. Edwin H. Barton's Article "Range and Sharpness of Resonance under Sustained Forcing and their Variations with Pitch" \*.* By Prof. Dr. E. WAETZMANN, of the Physical Institute of the University of Breslau †.

IN the above mentioned article Prof. E. H. Barton treats at length the damping of resonators, and discusses in particular the difference between the damping coefficient and the logarithmic decrement. In the introduction to his article Prof. Barton says: "It may be noted here that several writers have shown that the character of the resonance is a function of the responding system. But the decrement appears to have been treated as a single quantity measuring the damping. The possibility of changing the logarithmic decrement and therefore the sharpness of resonance, by a change in frequency, the damping coefficient remaining constant, seems to have escaped their attention."

I entirely agree with Prof. Barton in the opinion that

\* Phil. Mag. No. 151, July 1913.

† Communicated by the Author.

the word damping is often used in a sense not sufficiently clearly defined. When, however, he implies that the variation of the sharpness of resonance with a change in pitch, the coefficient of resonance remaining constant, has hitherto been disregarded, I beg leave to offer a slight correction. In several works on the resonance-theory of hearing\* I have suggested essentially the same definitions and distinctions with regard to damping that Prof. Barton now offers. I have in particular frequently availed myself of the fact that the sharpness of resonance, the coefficient of damping remaining constant, increases with the proper frequency of the resonator.

Whereas Helmholtz in his theory of hearing assumes that all the resonators of the ear have the same logarithmic decrement, that they have, therefore, disregarding certain negligible factors, the same sharpness of resonance, I have suggested and critically examined the hypothesis that it is not the logarithmic decrement, but rather the damping coefficient of all the resonators of the ear for the ordinary compass of the audible scale, which remains approximately the same.

In working out this theory I have calculated quantitatively the dependence of the sharpness of resonance on the proper frequency of the resonator, and should like to remark in this connexion, that all observed facts which have come to my notice agree better with my theory than with that of Helmholtz.

#### LIII. *On the Intrinsic Optical Activity of Isotropic Media.*

By G. H. LIVENS†.

**T**HERE are three different possible forms of the electron theory of the intrinsic optical rotatory power found to be associated with certain substances; the first is that given by Drude in his *Optik* (ch. vi.); the second is a mixture of this one and the third, which was developed by the author, following a suggestion from Prof. Lorentz‡. The object of the present paper is to decide which of these three satisfies most satisfactorily the test of experiment. Such a decision

\* E. Waetzmann, *Die Resonanztheorie des Hörens als Beitrag zur Lehre von den Tonempfindungen*, Vieweg u. Sohn, Braunschweig, 1912; *Bemerkung über die Dämpfung der Ohr-resonatoren*, Sitzung der Schlesischen Gesellschaft vom 28 Mai, 1913.

† Communicated by the Author.

‡ Livens, *Phil. Mag.* June 1913.



appears to have a fundamental bearing on the explanation of the real cause of the phenomenon.

There are two decisive tests which can be applied to the results of any theory; the formula it furnishes for the specific rotation of any substance must indicate clearly the dependence of this quantity on the density and aggregate constitution of that substance, and also on the frequency of the light used. The second test is probably the more fundamental, as there are probable actions of an entirely foreign nature which may mask the application of the first.

I need not here enter into the particular form in which the first test is to be applied, as I have examined the question thoroughly in previous communications\*.

The usual empirical formula found necessary to express the dependence of the rotation  $\omega$  on the frequency  $n$  of the light used, is one suggested by Boltzmann,

$$\omega = An^2 + Bn^4 + \dots$$

According to Landolt†, however, this formula, although fairly satisfactory in most cases, is not applicable to all of them. The formula suggested by Lommel,

$$\omega = \frac{An^2}{(n_r^2 - n^2)^2},$$

appears, however, to suit all cases so far known.

Now let us examine the three theories and the formulæ deduced from them. In all the various branches of the theory the all important relation is that connecting the electric force  $E$  with the electric flux density  $D$ , a relation which depends essentially on the constitution of the medium. It is, as usual, obtained, after Drude, by a statistical analysis of the motions of the contained electrons, to which the part of the electric flux due to the presence of the medium is due. These electrons are supposed to be connected to the molecules of the medium by quasi-elastic forces, and resisted in their motion by frictional forces proportional to their velocity. In the present discussion we shall, however, neglect the latter forces, so that the equations of motion of the electrons are of a type

$$m(\ddot{x} + n_r^2 x) = eF_x,$$

wherein  $(x, y, z)$  are the component displacements of the electron from its position of rest,  $m$  is its mass, and  $e$  the

\* Livens, Phil. Mag. June, September 1913.

† 'Das Optische Drehungsvermögen' (Brunswick, 1898), p. 126.



charge on it;  $mn_r^2$  is the parameter of the quasi-elastic force, and  $F$  the force on the contained electron due to the electric field in the incident wave.

We treat always the standard case of the propagation of plane waves of light of frequency  $n$  along the axis of  $z$ , so that all the functions depend on  $t$  and  $z$  by the factor

$e^{in(t - \frac{\mu}{c}z)}$  where  $\mu$  is the index of refraction of the medium for the light used, and  $c$  the velocity of radiation *in vacuo*. In such cases each electron will vibrate more or less freely with a period  $n$ , so that  $\ddot{x} = -n^2x$ , and therefore also

$$x = \frac{e/m}{n_r^2 - n^2} F_x;$$

and if  $P$  is the polarization intensity in the medium we know that  $P_x = \sum ex$ , and we therefore deduce that, vectorially,

$$P = \left( \sum \frac{e^2/m}{n_r^2 - n^2} \right) F.$$

the sum being taken per unit volume over all contained electrons. This is the fundamental relation from which all the circumstances of the propagation of the plane wave above specified are deduced.

What is the interpretation of  $F$ ? This is where the theories differ, and we cannot do better than examine them in turn, taking each on its merits.

1. *Drude's Theory*.—In the simple dispersion theory for isotropic media Drude simply takes

$$F = E,$$

so that when he desires to extend the theory and to introduce terms representing the effect of the asymmetric constitution of a naturally active medium, he can admit in  $F$  only terms depending simply on the differentials of the electric force components. He takes, in fact, in this general case,

$$F = E + b \text{ curl } E,$$

the second term on the right being of course merely a second order term whose form is determined and justified by the fundamental characteristics of the phenomena under review.

As I understand such a theory, it represents the optically active substance as modifying by its presence the ordinary structure of the æther, thereby imparting to it a slight secondary chiral structure.

If we adopt this form for  $\mathbf{F}$  then we deduce from above that

$$\begin{aligned} \mathbf{P} &= \left( \sum \frac{e^2/m}{n_r^2 - n^2} \right) (\mathbf{E} + b \operatorname{curl} \mathbf{E}) \\ &= a_1 \mathbf{E} + b_1 \operatorname{curl} \mathbf{E}. \end{aligned}$$

With this relation it can easily be verified that the two kinds of circularly polarized light are propagated with different velocities, which are respectively the roots of the two equations

$$\mu^2 - 1 - a_1 \pm \frac{\mu n b_1}{c} = 0,$$

and the combination of these two circularly polarized beams leads, as usual, to a pencil of linearly polarized light, whose plane of polarization is being rotated at a rate per unit length

$$\omega = \frac{1}{2} (\mu_+ - \mu_-) n,$$

which is

$$= \frac{n^2 b_1}{2c} = \frac{n^2}{2c} \sum \frac{b e^2/m}{n_r^2 - n^2}.$$

This is the ordinary formula obtained by Drude.

This formula appears very inadequate when the first test of constitution is applied to it, as witness the almost innumerable number of hypotheses introduced to explain the departures from it in the actual behaviour of most substances. It does not satisfy the second test very well, as the Boltzmann formula alone may be regarded as an approximation to it in certain very special cases.

2. *First modified theory.*—We have, however, seen that even in the simple case of ordinary isotropic media the term  $\mathbf{E}$  does not completely represent the whole effect of the force on the electron due to the applied field. We must, in fact, add a term  $a\mathbf{P}$ , where  $\mathbf{P}$  is, as before, the intensity of polarization induced in the medium, and  $a$  is a constant approximately equal to  $1/3$  in numerical value.

We are, however, still at liberty, when extending the theory to optically active substances, to assume the same origin for the chiral quality in the medium; and we should then have as a general form for  $\mathbf{F}$

$$\mathbf{F} = \mathbf{E} + a\mathbf{P} + b \operatorname{curl} \mathbf{E},$$

which would give a relation of the same form as before

$$P = a_1 E + b_1 \text{curl } E,$$

but in which

$$a_1 = \frac{\sum \frac{e^2/m}{n_r^2 - n^2}}{1 - \sum \frac{ae^2/m}{n_r^2 - n^2}}, \quad b_1 = \frac{\sum \frac{be^2/m}{n_r^2 - n^2}}{1 - \sum \frac{ae^2/m}{n_r^2 - n^2}},$$

and, therefore, on such a theory

$$\omega = \frac{n^2}{2c} \frac{\sum \frac{be^2/m}{n_r^2 - n^2}}{1 - \sum \frac{ae^2/m}{n_r^2 - n^2}}.$$

This formula, although slightly more general than the simple Drude formula, appears equally inadequate in both the fundamental tests.

3. *Second modified theory.*—In the complete form of the theory due to Lorentz it is, however, shown that the force on a contained electron must be represented in the general case by

$$F = E + f(P)^*,$$

where  $f(P)$  denotes some undetermined vector function of the polarization  $P$  of the medium, the first approximation to which is, however,  $aP$ , as above. In second order phenomena of the kind under discussion other terms may arise, and it is in these second order terms that Lorentz presumes the asymmetric structure to present itself.

It is therefore assumed that the next approximation in isotropic optically active media is

$$f(P) = aP + b \text{curl } P,$$

so that

$$F = E + aP + b \text{curl } P.$$

This assumption appears reasonable, in so far as it merely ascribes the observed chiral effect to the asymmetric structure of the various parts of the substance, without presuming any result of the effect of such a structure on the surrounding æther.

This relation has been shown by the author to lead to a

\* 'Versuch einer Theorie,' &c. (Leipzig, 1906), pp. 78-81.

formula for  $\omega$  of the form

$$\omega = \frac{n^2}{2} \frac{\left(\sum \frac{be^2/m}{n_r^2 - n^2}\right) \left(\sum \frac{e^2/m}{n_r^2 - n^2}\right)}{\left(1 - \sum \frac{ae^2/m}{n_r^2 - n^2}\right)^2},$$

and it appears to satisfy the two tests so well that there can hardly be any doubt as to its correctness. I have shown in my previous communications, how well it explains most of the variations observed in the specific rotation of a solution consequent on a variation of the constitution of that solution, and although one or two small difficulties were then met with, they may be overcome by the introduction of the effects due to more or less absorption of the light. This formula satisfies the second test equally well. In fact Lommel's formula is precisely the formula furnished by the present theory as a first approximation in the particular case where there is only one absorption band in the whole spectrum of the substance at an appreciable distance from the position in the spectrum corresponding to the frequency  $n$ .

It would, therefore, appear that the test of reality results entirely in favour of the third theory, and the formula deduced from it may therefore be taken as best representing the facts.

It may, of course, be argued that all three theories are the same in the end; it is only a matter of constants! However, when, as in the present case, the chief object is to investigate the nature of these constants, it is very essential that we should have a clear view of the form in which they are first introduced into the theory, the ultimate object being to obtain an explanation of their existence at all, in the form finally adopted for them.

Sheffield, Nov. 1913.

#### LIV. *On the Long-Wave Limits of the Normal Photoelectric Effect.*

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,

IN the December issue of the Philosophical Magazine, Drs. Pohl and Pringsheim discussed the present position of certain questions in photo-electricity, and concluded that there was not sufficient evidence to determine the relation between the maximum emission velocity of photo-electrons and the frequency of the light. It has long been



known that the velocity of the photo-electrons increases with the frequency of the light. Two laws have been proposed for the relation between the velocity and the frequency, the first being that the velocity squared, or the energy, of the photo-electron is proportional to the frequency, that is

$$V = kn - V_0, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $V$  is the potential difference required to stop the photo-electron, and therefore proportional to its energy, and  $n$  the frequency. The second is that the velocity is directly proportional to the frequency, or,

$$\sqrt{V} = k'n - c. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

On account of the small ranges of wave-lengths available it is difficult to decide which is the correct relation, but I think that Richardson & Compton's investigations and mine show undoubtedly that the results are well expressed by (1) but not by (2). Drs. Pohl and Pringsheim, in support of their contention that experiment has not decided between the two laws suggested, refer to experiments by Kunz and his pupil Cornelius, who conclude that their results are better expressed by equation (2). The experimental arrangements of Kunz and Cornelius are open to considerable objections, as has been pointed out very clearly by Compton (*Phys. Rev.* (2) i. p. 382, 1913), and it is therefore doubtful whether their results are of any value in deciding the exact nature of the relation between the velocity and the frequency. The experiments of Richardson and Compton and my experiments are the only experiments on this problem in which the measurements were sufficiently accurate to distinguish between the proposed relations (1) and (2), and both investigations lead to the conclusion that (1) is the true relation. Drs. Pohl and Pringsheim offer several objections to these researches, the first being that the intensity of the shortest wave-length used (especially in my experiments) was so feeble that the illuminated plate would never charge up to its proper potential on account of insulation leaks. The method used in my experiments was practically a null method, so that this objection has but little weight. In this connexion they state that errors may arise from light being diffused to the electrode surrounding the illuminated plate. The amount of light which gets through the monochromator, other than the isolated wave-length, is quite small, and by the time a fraction of it is reflected by the illuminated plate to the surrounding electrode, the effect is negligible. This could be shown by a simple control experiment.

Drs. Pohl and Pringsheim have found that the long wave-length limit of the photo-electric effect for some of the metallic surfaces prepared by them shifts a considerable distance along the spectrum during the course of a few hours after the formation of the surface. This interesting result does not tell us anything about the relation between  $V$  and  $n$ ; all that it does is to show that  $V_0$  in equation (1) probably alters with the course of time. It is probable that if they measured the emission velocity of the photo-electrons while the surfaces of the metals were changing, they would find that the relation between the velocity and the frequency was always represented by (1) and that the line corresponding to (1) moved parallel to itself as the long wave-length limit moved towards the red end of the spectrum. This is a point to be decided by experiment.

Yours truly,  
A. LL. HUGHES.

The Rice Institute,  
Houston, Texas.  
Dec. 24th, 1913.

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LV. *On the Distribution of Energy in the Spectra of Gases.*

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

IN Mr. H. L. P. Jolly's paper on the Distribution of Energy in the Spectra of Gases in the *Philosophical Magazine* for November 1913, there is to be found a summary of previous work on the subject, from which several papers published by myself or pupils of mine on the same subject are missing. May I be allowed to mention those papers for the benefit of the readers of your Journal:—

H. Konen and W. Jungjohann, "Studies on the Emission of Gases," *Astrophys. Journ.* xxxi. pp. 404-418 (1910).  
H. Konen and W. Jungjohann, "Studies on the Emission of Gases, II.," *ib.* xxxii. pp. 141-152 (1910).  
W. Jungjohann, "Ueber Emission und Absorption leuchtender Gase bei hohen Stromdichten unter Verwendung von Gleichstrom," *Zeitschr. f. wiss. Photographie &c.* ix. pp. 84-103, 105-168 (1910).  
H. Kyll, "Intensitätsmessungen im positiven Bandenspectrum des Stickstoffs," Dissertation, Münster, 1910.  
J. Schwedes, "Ueber Intensitätsmessungen strömender Gase bei hohen Stromdichten unter Verwendung von Gleichstrom," *Zeitschr. f. wiss. Photographie &c.* xi. pp. 169-204 (1912).

H. Konen, "das Leuchten der Gase und Dämpfe," Braunschweig, 1913, pp. 302 ff. Besides many papers by other authors not mentioned in Mr. Jolly's summary.

From the experience gained in our Münster Laboratory it seems necessary:

- (1) to make use of tubes with a *continuous flow of gas*;
- (2) to make use of *continuous electric current* in all measurements of intensity or energy of spectral lines in order to avoid complications that make it impossible to draw any reliable conclusions either from radiometric or photometric measurements. That it is possible to fulfil both conditions, by means of special tubes described in the first of the papers mentioned above, is, in my opinion, conclusively shown by Mr. J. Schwedes.

Yours very truly,

H. KONEN.

Münster i/W, physikalisches Institut  
der Universität, Jan. 25, 1914.

LVI. *The Theory of Photoelectric and Photochemical Action.*

By O. W. RICHARDSON, F.R.S., *Wheatstone Professor of Physics, University of London, King's College*\*.

FOR many reasons and especially on account of the complexity which recent experimental investigations † have shown to characterize the relation between the number of electrons emitted by bodies and the intensity and frequency of the radiation used to stimulate them, it seems desirable to consider the theory of these effects from as many points of view as possible. I have therefore amplified the discussion of some of the points raised in my previous papers dealing with these questions. I shall consider first the amount of energy which is abstracted from the radiation when one electron or atom is liberated. In what follows immediately I shall use the term atom to include electrically charged particles, *i. e.* ions and electrons, since the argument is exactly the same whether the particles are supposed electrically charged or not.

\* Communicated by the Author. A paper read before the American Physical Society at the Chicago Meeting, Nov. 28, 1913.

† Pohl and Pringsheim, numerous papers in recent volumes of the *Verhandlungen der Deutschen Physik. Gesellschaft*. Compton and Richardson Phil. Mag. vol. xxvi. p. 549 (1913).

*The Energy abstracted per Atom liberated.*

Consider any condensed form of any substance, bounded by a surface, which emits any monatomic gas under the influence of illumination.

Let  $\xi$  = the mean internal kinetic energy of these atoms, *i. e.* the kinetic energy they possess when in the condensed form.

$W$  = the average work done by each atom in escaping from the substance.

$w$  = the average change of total energy which accompanies the escape of a single atom.

Then  $\frac{3}{2} RT$  is the mean external kinetic energy (*i. e.* after escaping) of an atom at temperature  $T$  and

$$w = \frac{3}{2} RT - \xi + W. \quad . \quad . \quad . \quad . \quad (1)$$

Let  $\phi(\nu)$  denote the mean energy which each atom, liberated under the influence of monochromatic radiation of frequency  $\nu$ , has acquired from the radiation at the moment of liberation. The kinetic energy of each atom immediately before emission is thus  $\phi(\nu) + \xi$ , if the contribution to  $\xi$  arising from the radiation is treated as negligible (see last paragraph), and the mean kinetic energy each atom carries away from the surface of the substance is

$$T_\nu = \phi(\nu) + \xi - W = \phi(\nu) + \frac{3}{2} RT - w. \quad . \quad . \quad (2)$$

If the substance is enclosed by an isolating boundary, so that the space between the substance and the boundary is initially vacuous, there will ultimately be equilibrium characterized by some constant temperature, let us say  $T$ . The body will be emitting atoms under the influence of the complete radiation characteristic of  $T$ , and these will be returning to the body on account of their kinetic motions. The two processes balance, so that the state is invariable. By moving a piston transparent to radiation, the quantity of emitted gas can be varied without changing the quantity of radiation, so that, as before\*, if  $n$  is the number of liberated atoms per unit volume,

$$n = A_0 e^{\int_{RT^2}^T w dT}, \quad . \quad . \quad . \quad . \quad (3)$$

where  $A_0$  is a quantity which is characteristic for the substance but is independent of  $T$ . The number  $N_1$  of liberated

\* O. W. Richardson, *Phil. Mag.* vol. xxiii. p. 619 (1912).



atoms which are returned to each unit area of the substance in unit time is

$$N_1 = n \beta T^{\frac{3}{2}} = A T^{\frac{3}{2}} e^{\int \frac{w}{RT^2} dT}, \dots \dots \dots (4)$$

where  $\beta$  is a constant readily calculated from the kinetic theory of gases and  $A$  is thus still independent of  $T$  and characteristic for the substance.

Let  $\epsilon F(\nu)$  be the number of atoms emitted from unit area of the substance in unit time in the presence of unit energy density of frequency between  $\nu$  and  $\nu + d\nu$ , and assume that the number of atoms emitted in the presence of the whole spectrum characteristic of  $T$  is, using Planck's formula,

$$N_2 = \frac{C}{4} \frac{8\pi}{C^3} \int_{\nu_0}^{\infty} \epsilon F(\nu) \frac{h\nu^3}{e^{\frac{h\nu}{RT}} - 1} d\nu. \dots \dots (5)$$

This equation contains the important assumption, which does not yet seem to have tested experimentally, that the number of atoms emitted by a given amount of light is the same whether the light is undecomposed or is broken up, without loss of energy, into its spectral constituents. In other words, it assumes that the photochemical substance acts as its own grating. This may be justified as being the simplest assumption which is consistent with the conclusions drawn from experiments on photoelectric action, that the number of emitted electrons is simply proportional to the intensity of light of definite spectral composition but varies greatly when equal energies of light of different frequencies are compared.

In (5) we have taken the lower limit of the integral to be finite and equal to  $\nu_0$ . This is to cover the possibility, which appears to be demanded by the results of photoelectric experiments, that  $\epsilon F(\nu)$  is a function which takes the value zero when  $\nu = \nu_0$  and does not exist for values of  $\nu$  between 0 and  $\nu_0$ . If  $\epsilon F(\nu)$  is a function which extends over the whole spectrum the case can be provided for by simply putting  $\nu_0 = 0$ .

Now consider the kinetic energy which is carried away from the substance by the atoms liberated under the influence of the radiation. If  $\epsilon F(\nu)$  has the properties we have attributed to it, this amount of kinetic energy is, by virtue of (2) and (5),

$$E_2 = \frac{2\pi}{c^3} \int_{\nu_0}^{\infty} \left\{ \phi(\nu) + \frac{3}{2} RT - w \right\} \epsilon F(\nu) \frac{h\nu^3}{e^{\frac{h\nu}{RT}} - 1} d\nu \dots (6)$$

$$= \frac{2\pi}{c^3} \int_{\nu_0}^{\infty} \phi(\nu) \epsilon F(\nu) \frac{h\nu^3}{e^{\frac{h\nu}{RT}} - 1} d\nu - N_2 \left( w - \frac{3}{2} RT \right). \quad (7)$$

We have also from (5)

$$RT^2 \frac{\partial N_2}{\partial T} = \frac{2\pi}{c^2} \int_{\nu_0}^{\infty} \left\{ \frac{h\nu e^{\frac{h\nu}{RT}}}{e^{\frac{h\nu}{RT}} - 1} + RT^2 \frac{\partial \log \epsilon F(\nu)}{\partial T} \right\} \frac{\epsilon F(\nu) h\nu^3}{e^{\frac{h\nu}{RT}} - 1} d\nu, \quad (8)$$

since  $\epsilon F(\nu) = 0$  when  $\nu = \nu_0$ .

Differentiating (4) by  $T$ , we have

$$\begin{aligned} RT^2 \frac{\partial N_1}{\partial T} &= N_1 \left( \frac{R}{2} T + w_T \right), \\ &= E_1 + N_1 \left( w_T - \frac{3}{2} RT \right), \quad . . . . \quad (9) \end{aligned}$$

where  $E_1 = 2N_1RT$  is the kinetic energy returned to the substance by the motion of thermal agitation of the gas. In the steady state  $E_1 = E_2$  and  $N_1 = N_2$ . This is true, so far as the present use of these equations is concerned, even if there is scattering or reflexion of atoms at the surface of the substance. For by a well-known principle in atomic statistics there are as many deflexions of returning atoms outwards, of a given class, as there are deflexions inwards of escaping atoms of the same class. Substituting for  $E_1$  and  $N_1$  in (9) the values given by (7) and (8) we get

$$\int_{\nu_0}^{\infty} \frac{\epsilon F(\nu) h\nu^3}{e^{\frac{h\nu}{RT}} - 1} \left\{ \phi(\nu) - \frac{h\nu e^{\frac{h\nu}{RT}}}{e^{\frac{h\nu}{RT}} - 1} - RT^2 \frac{\partial \log \epsilon F(\nu)}{\partial T} \right\} d\nu = 0. \quad (10)$$

This equation is true for all values of  $\nu_0$  and  $T$  and for all the admissible forms of  $\epsilon F(\nu)$  characteristic of different substances. In general it appears from (10) that  $\phi(\nu)$  may be dependent not only on  $\nu$  but may also involve the properties of the substance, through  $\epsilon F(\nu)$  and  $\nu_0$  and the temperature  $T$ . The experimental evidence all goes to show that at sufficiently low temperatures photoelectric action is approximately independent of the temperature of the substance for light of a given intensity; so that at low temperatures (such for example as are employed in ordinary laboratory experiments on these effects) equation (10) reduces to

$$\int_{\nu_0}^{\infty} \epsilon F(\nu) h\nu^3 e^{-\frac{h\nu}{RT}} \{ \phi(\nu) - h\nu \} d\nu = 0. \quad . . \quad (11)$$

If photochemical and photoelectric actions are (fundamentally) independent of temperature at low temperatures then  $\epsilon F(\nu)$  and  $\phi(\nu)$  will be functions of  $\nu$  and  $\nu_0$  only and will not involve  $T$ . In that case either  $\epsilon F(\nu) = 0$  or  $\phi(\nu) = h\nu$

for every value of  $\nu$ . For it is easy to show that the only regular function of  $\nu$  not involving  $T$  which satisfies the equation

$$\int_{\nu_0}^{\infty} \chi(\nu) e^{-\frac{h\nu}{RT}} d\nu = 0, \quad . \quad . \quad . \quad . \quad (12)$$

if  $\nu_0$  is also independent of  $T$ , is  $\chi(\nu) = 0$ . For let

$$\chi(\nu) = a_0 + \sum_{s=1}^{\infty} a_s \nu^s + b_s \nu^{-s}$$

over the range  $\nu_0 < \nu < \infty$ . By repeated integration of (12) with respect to  $dT$  from 0 to  $T$  or repeated differentiation with respect to  $T$ , we see that for every integer  $p$

$$\int_{\nu_0}^{\infty} \nu^{\pm p} \chi(\nu) e^{-\frac{h\nu}{RT}} d\nu = 0. \quad . \quad . \quad . \quad . \quad (13)$$

Multiplying the integrals (13) by the corresponding constants  $a_0 a_1 a_2 \dots b_1 b_2 \dots$  and adding we get

$$\int_{\nu_0}^{\infty} [\chi(\nu)]^2 e^{-\frac{h\nu}{RT}} d\nu = 0.$$

Since  $e^{-\frac{h\nu}{RT}}$  and  $\nu_0$  are always positive it follows that  $\chi(\nu) = 0$  for  $\nu_0 < \nu < \infty$ . Applying this result to (11) it follows that

$$\phi(\nu) = h\nu. \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Thus the quantity of energy which an atom abstracts from the radiation before it is liberated, under the influence of light of frequency  $\nu$ , is  $h\nu$ .

This result has only been shown to be valid at low temperatures. It appears to follow from the following assumptions:—

- (1) That the distribution of energy in the radiation is given by Planck's formula.
- (2) That such a function as  $\epsilon F(\nu)$  exists and the effects of the spectral components of mixed light are additive.
- (3) That photochemical actions are fundamentally independent of temperature at low temperatures and that they do not contravene the second law of thermodynamics.
- (4) That the part of  $\xi$  which comes from the radiation is negligible.

This demonstration shows that the considerations about the specific heat of electricity and electron reflexion which entered into proofs \* I have given of this and related formulæ

\* Phys. Rev. vol. xxxiv. p. 146 (1912); Phil. Mag. vol. xxiii. p. 624 (1912), vol. xxiv. p. 570 (1912).

were not really essential. Equation (14) has also been obtained by Einstein \*, who bases his demonstration on the assumption that radiation of the same frequency and equal amount as that absorbed during emission is given out on recombination. This hypothesis seems to be of a restrictive character and results in the existence of states of radiation in equilibrium with matter which are different from the complete radiation characteristic of that temperature. The justification urged for the existence of such states of equilibrium between matter and radiation is that they would not violate the second law of thermodynamics. It appears, however, from the foregoing considerations that the particular limitation set up by Einstein is not really essential.

In a recent paper Planck † has considered the equilibrium between radiation and matter which liberates electrons under its influence. He arrives thus at a consistent system which includes Planck's law of distribution for the radiant energy and Maxwell's law for the energy of the electrons. The law which Planck finds to govern the amount of energy abstracted from the radiation by the liberated electrons agrees with that found above in that it approaches  $h\nu$  as the temperature approaches zero. This follows from equations (12) and (28) of Planck's paper.

Einstein's demonstration leads to (14) as a limit which is true for small radiation densities. This may be regarded as analogous to the result obtained above, according to which (14) is necessarily valid only at low temperatures; since low temperatures correspond to small radiation densities.

It is evident from what has been said that the functions  $\chi(\nu, \nu_0, T)$  which satisfy the equation

$$\int_{\nu_0}^{\infty} \frac{\nu^3}{e^{\frac{h\nu}{RT}} - 1} \chi(\nu_1, \nu_0, T) d\nu = 0 \quad . \quad . \quad (15)$$

are of great interest in the theory of photochemical action.

It will be observed that we have not proved that (14) is not true at all temperatures. All we have proved is that if photochemical action is fundamentally independent of temperature at low temperatures, then at such temperatures (14) is true. I shall show in a moment that a consistent

\* *Ann. der Physik*, vol. xxxvii, p. 832 (1912); *Journ. de Physique*, 1913.

† *Sitzungsber. der k. Preuss. Akad. der Wiss., Physik.-Math. Classe*, xviii. p. 350 (1913).



$$\phi(\nu) = h\nu$$

universally, at all temperatures. The deduction will depend on assumptions (1), (2), and (4) but not on the first part of assumption (3).

*The Amount of Decomposition.*

The function  $\epsilon F(\nu)$  is of great interest. The experiments on photoelectric action show that it may be very complicated, and the simple solutions of the equations which I have so far been able to consider exhibit only a rough correspondence with the experimental results\*. It is, however, important to know whether they are affected by the considerations about the specific heat of electricity which I have previously made use of.

$\epsilon F(\nu)$  is a function of  $\nu_0$  as well as  $\nu$ . Let us denote it by  $F(\nu_0, \nu)$ . Then from (4) and (5),

$$\frac{2\pi}{c^2} \int_{\nu_0}^{\infty} \frac{h\nu^3}{e^{\frac{h\nu}{RT}} - 1} F(\nu_0, \nu) d\nu = AT^{\frac{3}{2}} e^{\int_{\nu_0}^T \frac{w}{RT^2} dT} = N. \quad (16)$$

This equation may be varied by giving to  $w$  a small increment  $\eta$  (independent of  $T$ ) and a corresponding increment  $\xi$  to  $\nu_0$ , the other quantities being unchanged. This variation is admissible because it can be realized physically by making use of a layer of attracting matter or an electrical double layer. Hence

$$\int_{\nu_0 + \xi}^{\infty} \frac{h\nu^3}{e^{\frac{h\nu}{RT}} - 1} F(\nu_0 + \xi, \nu) d\nu = e^{-\frac{\eta}{RT}} \int_{\nu_0}^{\infty} \frac{h\nu^3 F(\nu_0, \nu)}{e^{\frac{h\nu}{RT}} - 1} d\nu.$$

Neglecting squares and higher powers of the small quantities  $\xi, \eta$ , and remembering that  $F(\nu_0, \nu) = 0$  when  $\nu = \nu_0$ , this gives

$$\int_{\nu_0}^{\infty} \frac{h\nu^3}{e^{\frac{h\nu}{RT}} - 1} \left\{ \frac{\eta}{RT} F(\nu_0, \nu) + \xi \frac{\partial F(\nu_0, \nu)}{\partial \nu_0} \right\} d\nu = 0. \quad (17)$$

Equation (17) is solved by

$$\frac{\eta}{\xi} = h, \text{ and } F(\nu_0, \nu) = \frac{\text{const}}{\nu^3} \left( 1 - e^{-\frac{h\nu}{RT}} \right) \times (\nu - \nu_0)^p \quad (18)$$

where  $p$  is any positive number. This solution includes the

\* Compton and Richardson (*loc. cit.*).

one previously discussed \*, viz :—

$$\frac{\eta}{\xi} = h, \text{ and } F(\nu_0, \nu) = \frac{\text{const}}{\nu^3}(\nu - \nu_0) \dots \dots (19)$$

as the particular case  $p=1$  restricted in validity to small values of  $T$ .

Now consider the equation (16), which we may write

$$I = \int_{\nu_0}^{\infty} \frac{\nu^3 F(\nu_0, \nu)}{1 - e^{-h\nu/RT}} e^{-\frac{h\nu}{RT}} h d\nu = \Phi(T) e^{-\frac{h\nu_0}{RT}}, \dots (20)$$

where

$$\Phi(T) = AT^{\frac{1}{2}} e^{\frac{h\nu_0}{RT}} + \int \frac{\nu}{RT^2} dT \dots \dots (21)$$

This may be regarded as defining  $\Phi(T)$ . Equation (18) suggests putting

$$F(\nu_0, \nu) = \frac{1}{\nu^3} (1 - e^{-\frac{h\nu}{RT}}) \psi(\nu - \nu_0), \dots \dots (22)$$

where  $\psi$  is an undetermined function of  $\nu - \nu_0$  only and does not involve  $T$ . It follows from (18) that  $\psi$  can include every function of the argument which is regular between  $\nu = \nu_0$  and  $\nu = \infty$  and still be a solution of (17). By changing the variable to  $z = \frac{h(\nu - \nu_0)}{RT}$ ,

$$I = RT e^{-\frac{h\nu_0}{RT}} \int_0^{\infty} \psi\left(\frac{RT}{h}z\right) e^{-z} dz,$$

and by successive integration by parts

$$RT \left\{ \psi(0) + \frac{RT}{h} \psi'(0) + \left(\frac{RT}{h}\right)^2 \psi''(0) + \dots + \left(\frac{RT}{h}\right)^n \psi^n(0) + \dots \right\} = \Phi(T). \dots (23)$$

Since, by hypothesis  $\psi(\nu - \nu_0)$  does not depend on  $T$ ,  $\psi(0)$ ,  $\psi'(0)$  ...  $\psi^n(0)$  ... &c. are all independent of  $T$ . If the solution we are seeking exists, equation (23) must be true for all real positive values of  $T$ . The solution therefore will only exist if  $\Phi(T)$  can be expanded as a series of positive integral powers of  $T$ . By Maclaurin's theorem, if such an expansion is possible,

$$\Phi(T) = \Phi(0) + T\Phi'(0) + \frac{T^2}{2!} \Phi''(0) + \dots + \frac{T^n}{n!} \Phi^n(0) + \dots (24)$$

\* Phil. Mag. vol. xxiv. p. 570 (1912).

Hence by comparing coefficients,  $\Phi(0)=0$  and

$$\begin{aligned}\psi(0) &= \frac{1}{R} \Phi'(0), & \psi'(0) &= \frac{h}{R^2 2!} \Phi''(0), \dots, \\ \psi^{n-1}(0) &= \frac{h^{n-1}}{R^n n!} \Phi^n(0), \text{ \&c. } \dots \dots \dots (25)\end{aligned}$$

Since

$$\psi(x) = \psi(0) + x\psi'(0) + \frac{x^2}{2!}\psi''(0) + \dots \dots \dots (26)$$

the relations (25) are sufficient to determine  $\psi(v-v_0)$  if it exists.

Let us now consider the equation which expresses the balance of kinetic energy between the outgoing and returning streams of atoms. This may be written, using (2), (6), and (16), since  $E=2NRT$ ,

$$J = \int_{v_0}^{\infty} \frac{v^3 T_v F(v_0, v)}{e^{\frac{hv}{RT}} - 1} h dv = \frac{c^2}{\pi} NRT = 2RT\Phi(T)e^{-\frac{hv_0}{RT}}, \dots (27)$$

or

$$J = \int_{v_0}^{\infty} \chi(v-v_0)e^{-\frac{hv}{RT}} h dv = 2RT\Phi(T)e^{-\frac{hv_0}{RT}}, \dots (28)$$

if

$$\chi(v-v_0) \equiv T_v \psi(v-v_0) \dots \dots \dots (29)$$

is a function only of  $(v-v_0)$ . This assumption is suggested since the form of (28) is the same as that of (20). Thus, by the same treatment as in dealing with (20),

$$\begin{aligned}\chi(0) + \frac{RT}{h}\chi'(0) + \left(\frac{RT}{h}\right)^2\chi''(0) + \dots + \left(\frac{RT}{h}\right)^n\chi^n(0) + \dots &= 2\Phi(T) \\ &= 2RT\left\{\psi(0) + \left(\frac{RT}{h}\right)\psi'(0) + \left(\frac{RT}{h}\right)^2\psi''(0) + \dots + \left(\frac{RT}{h}\right)^n\psi^n(0) + \dots\right\}\end{aligned}$$

whence  $\chi(0)=0$  and

$$\chi'(0)/\psi(0) = \chi''(0)/\psi'(0) = \dots = \chi^n(0)/\psi^{n-1}(0) = \dots = 2h. \dots \dots (30)$$

Since  $\chi(x) = \chi(0) + x\chi'(0) + \frac{x^2}{2!}\chi''(0) + \dots$

$$\begin{aligned}&= 2h\left(x\psi(0) + \frac{x^2}{2!}\psi'(0) + \frac{x^3}{3!}\psi''(0) + \dots\right) \\ &= 2h\int_0^x \psi(x) dx = T_x \psi(x), \text{ from (29),}\end{aligned}$$

we see that

$$T_x = \frac{2h}{\psi(x)} \int_0^x \psi(x) dx \dots \dots \dots (31)$$

Now turn to the equation (21) which defines  $\Phi(T)$ . Differentiate both sides by  $T$  and divide each side of the resulting equation by the corresponding side of (21). This gives

$$w = h\nu_0 - \frac{RT}{2} + RT^2 \frac{\Phi'(T)}{\Phi(T)} \dots \dots \dots (32)$$

But, from equation (2),

$$\begin{aligned} T_\nu &= \phi(\nu) + \frac{3}{2} RT - w \\ &= \phi(\nu) - h\nu_0 + 2RT - RT^2 \frac{\Phi'(T)}{\Phi(T)}, \dots \dots (33) \end{aligned}$$

and since  $T_\nu$  is from (29) a function of  $\nu - \nu_0$  only, it follows from (33) that

$$\phi(\nu) = h\nu - 2RT + RT^2 \frac{\Phi'(T)}{\Phi(T)} + f(\nu - \nu_0)$$

where  $f(\nu - \nu_0)$  is an arbitrary function of  $\nu - \nu_0$  only. But  $f$  must be zero because  $\phi$  cannot involve  $\nu_0$  which depends on the properties of a distant surface. Thus

$$\phi(\nu) = h\nu - 2RT + RT^2 \frac{\Phi'(T)}{\Phi(T)} \dots \dots \dots (34)$$

Substituting the value of  $F(\nu_0, \nu)$  given by (22) in (10) we have

$$\int_{\nu_0}^{\infty} \psi(\nu - \nu_0) \{ \phi(\nu) - h\nu \} e^{-\frac{h\nu}{RT}} d\nu = 0,$$

and, from (34),

$$\left\{ RT^2 \frac{\Phi'(T)}{\Phi(T)} - 2RT \right\} \int_{\nu_0}^{\infty} \psi(\nu - \nu_0) e^{-\frac{h\nu}{RT}} d\nu = 0.$$

Since  $\psi(\nu - \nu_0) \neq 0$ ,

$$RT^2 \frac{\Phi'(T)}{\Phi(T)} - 2RT = 0 \dots \dots \dots (35)$$



From this

$$\Phi(T) = AT^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

where A is a constant, and from (34)

$$\phi(\nu) \equiv h\nu, \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

for every substance and at all temperatures. Thus the restriction to low temperatures which might have been required for (37) to satisfy (10) is not really necessary. Equation (33) now reduces to

$$T_\nu = h(\nu - \nu_0), \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

and, putting  $\nu - \nu_0 = x$ , (31) becomes

$$x\psi(x) = 2 \int_0^x \psi(x) dx, \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

or

$$x \frac{\partial \psi(x)}{\partial x} + \psi(x) = 2\psi(x). \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

Thus

$$\psi(\nu - \nu_0) = A_1(\nu - \nu_0), \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

where  $A_1$  is a constant. The values of  $\Phi$  and  $\psi$  given by (36) and (41) respectively satisfy the relations (25), since

$$\psi'(0) = A_1, \quad \Phi''(0) = 2A,$$

and all the other coefficients vanish. Incidentally, from (32),

$$w = h\nu_0 + \frac{3}{2}RT. \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

The results of this investigation may be summarized as follows :—Considering the equation

$$\int_{\nu_0}^{\infty} \frac{\nu^3 T_\nu F(\nu_0, \nu)}{e^{\frac{h\nu}{RT}} - 1} h d\nu = 2RT\Phi(T)e^{-\frac{h\nu_0}{RT}} = 2ART^{3/2} \int_0^{\frac{T}{T^2}} \frac{w}{T^2} dT,$$

which contains most of the quantities under discussion. This equation and equations (10), (16), and (17), all of which involve independent relationships, are all satisfied

by the following consistent scheme of mutually related functions:—

$$\left. \begin{aligned} \phi(\nu) &= h\nu, & 0 < \nu < \infty, \\ F(\nu_0, \nu) &= \frac{Ah}{R^2} \left( 1 - e^{-\frac{h\nu}{RT}} \right) \frac{\nu - \nu_0}{\nu^3}, & \nu_0 < \nu < \infty, \\ T_\nu &= h(\nu - \nu_0), & \nu_0 < \nu < \infty, \\ h\nu_0 &= w - \frac{3}{2} RT, \\ \Phi(T) &= AT^2. \end{aligned} \right\} \quad (43)$$

So far as I have been able to discover, this is the only set of functions involving only a single critical frequency which will satisfy all the relations as laid down (see below) without contradiction. No use whatever has been made of the value of the specific heat of electricity or any other specifically electrical property of the materials, so that the results will be just as valid for photochemical as for photoelectric actions.

A certain amount of caution is necessary in the application of these formulæ to compare with the results of experiments. In carrying out the calculations we have entirely neglected the part played by electron reflexion in the electrical case, and by the corresponding deflexions of the atoms in the types of photochemical action which are more generally regarded as such. From the principle of statistical equivalence referred to on p. 479, it follows that this neglect will not affect the equilibrium values, so that the equations (43) will express the relations which are inherent in the phenomena so far as the action of the radiation on the molecules is concerned. But in photoelectric experiments at any rate we have to deal, not with a state of equilibrium, but with the rate of emission under given illumination. This is less than the ideal emission by an amount which represents the number of electrons deflected back into the interior. An exactly similar difficulty arises in the application of the equilibrium theory of the thermionic emission of electrons to the experimental measurements of the maximum rate of thermionic emission at a given temperature\*.

More serious limitations are introduced by the assumption that the contribution to the mean internal kinetic energy  $\xi$  arising from the radiation is negligible. It is, in fact, possible that the whole of  $\xi$  may arise in this way. To

\* O. W. Richardson, *Phil. Mag.* vol. xxiii. p. 604 (1912).

include the possibility that the part of  $\xi$  thus arising is not negligible we might have defined  $\phi(\nu)$  rather differently as the excess at emission of the internal kinetic energy over the mean value  $\xi$ . In that case some of the other conclusions would require reconsideration. Also, the results which have been given are not easily harmonized with the values of the specific heats of bodies at low temperatures. For these reasons, the formulation outlined above is to be taken as illustrative rather than final. Another direction in which it is practically certain that the foregoing theory is too much simplified is in the assumption of only one critical frequency  $\nu_0$ . I hope to be able to return to the discussion of these questions later.

Palmer Physical Laboratory,  
Princeton, N. J.

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LVII. *The Structure of the Atom.* By SIR ERNEST RUTHERFORD, F.R.S., Professor of Physics, University of Manchester \*.

THE present paper and the accompanying paper by Mr. C. Darwin deal with certain points in connexion with the "nucleus" theory of the atom which were purposely omitted in my first communication on that subject (Phil. Mag. May 1911). A brief account is given of the later investigations which have been made to test the theory and of the deductions which can be drawn from them. At the same time a brief statement is given of recent observations on the passage of  $\alpha$  particles through hydrogen, which throw important light on the dimensions of the nucleus.

In my previous paper (*loc. cit.*) I pointed out the importance of the study of the passage of the high speed  $\alpha$  and  $\beta$  particles through matter as a means of throwing light on the internal structure of the atom. Attention was drawn to the remarkable fact, first observed by Geiger and Marsden †, that a small fraction of the swift  $\alpha$  particles from radioactive substances were able to be deflected through an angle of more than  $90^\circ$  as the results of an encounter with a single atom. It was shown that the type of atom devised by Lord Kelvin and worked out in great detail by Sir J. J. Thomson was unable to produce such large deflexions unless the diameter of the positive sphere was exceedingly small. In order to account for this large angle scattering of  $\alpha$  particles, I supposed that the atom consisted of a positively charged nucleus of small dimensions

\* Communicated by the Author.

† Proc. Roy. Soc. A. lxxxii. p. 495 (1909).

in which practically all the mass of the atom was concentrated. The nucleus was supposed to be surrounded by a distribution of electrons to make the atom electrically neutral, and extending to distances from the nucleus comparable with the ordinary accepted radius of the atom. Some of the swift  $\alpha$  particles passed through the atoms in their path and entered the intense electric field in the neighbourhood of the nucleus and were deflected from their rectilinear path. In order to suffer a deflexion of more than a few degrees, the  $\alpha$  particle has to pass very close to the nucleus, and it was assumed that the field of force in this region was not appreciably affected by the external electronic distribution. Supposing that the forces between the nucleus and the  $\alpha$  particle are repulsive and follow the law of inverse squares, the  $\alpha$  particle describes a hyperbolic orbit round the nucleus and its deflexion can be simply calculated.

It was deduced from this theory that the number of  $\alpha$  particles falling normally on unit area of a surface and making an angle  $\phi$  with the direction of the incident rays is proportional to

- (1)  $\text{cosec}^4 \phi/2$  or  $1/\phi^4$  if  $\phi$  be small ;
- (2) the number of atoms per unit volume of the scattering material ;
- (3) thickness of scattering material  $t$  provided this is small ;
- (4) square of the nucleus charge  $Ne$  ;
- (5) and is inversely proportional to  $(mu^2)^2$ , where  $m$  is the mass of the  $\alpha$  particle and  $u$  its velocity.

From the data of scattering on  $\alpha$  particles previously given by Geiger \*, it was deduced that the value of the nucleus charge was equal to about half the atomic weight multiplied by the electronic charge. Experiments were begun by Geiger and Marsden † to test whether the laws of single scattering of  $\alpha$  particles were in agreement with the theory. The general experimental method employed by them consisted in allowing a narrow pencil of  $\alpha$  particles to fall normally on a thin film of matter, and observing by the scintillation method the number scattered through different angles. This was a very difficult and laborious piece of work involving the counting of many thousands of particles. They found that their results were in very close accord with the theory. When the thickness of the scattering film was very small, the amount of scattering was directly proportional

\* Proc. Roy. Soc. A. lxxxiii. p. 492 (1910).

† Geiger and Marsden, Phil. Mag. xxv. p. 604 (1913).



to the thickness and varied inversely as the fourth power of the velocity of the incident  $\alpha$  particles. A special study was made of the number of  $\alpha$  particles scattered through angles varying between  $5^\circ$  and  $150^\circ$ . Although over this range the number decreased in the ratio 200,000 to 1, the relation between number and angle agreed with the theory within the limit of experimental error. They found that the scattering of different atoms of matter was approximately proportional to the square of the atomic weight, showing that the charge on the nucleus was nearly proportional to the atomic weight. By determining the number of  $\alpha$  particles scattered from thin films of gold, they concluded that the nucleus charge was equal to about half the atomic weight multiplied by the electronic charge. On account of the difficulties of this experiment, the actual number could not be considered correct within more than 20 per cent.

The experimental results of Geiger and Marsden were thus in complete accord with the predictions of the theory, and indicated the essential correctness of this hypothesis of the structure of the atom.

In determining the magnitude of single scattering, I assumed in my previous paper, for simplicity of calculation, that the atom was at rest during an encounter with an  $\alpha$  particle. In an accompanying paper, Mr. C. Darwin has worked out the relations to be expected when account is taken of the motion of the recoiling atom. He has shown that no sensible error has been introduced in this way even for atoms of such low atomic weight as carbon. Mr. Darwin has also worked out the scattering to be expected if the law of force is not that of the inverse square, and has shown that it is not in accord with experiment either with regard to the variation of scattering with angle or with the variation of scattering with velocity. The general evidence certainly indicates that the law of force between the  $\alpha$  particle and the nucleus is that of the inverse square.

It is of interest to note that C. T. R. Wilson \*, by photographing the trails of the  $\alpha$  particle, later showed that the  $\alpha$  particle occasionally suffers a sudden deflexion through a large angle. This affords convincing evidence of the correctness of the view that large deflexions do occasionally occur as a result of an encounter with a single atom.

On the theory outlined, the large deflexions of the  $\alpha$  particle are supposed to be due to its passage close to the nucleus where the field is very intense and to be not appreciably affected by its passage through the external distribution of

\* C. T. R. Wilson, Proc. Roy. Soc. A. lxxxvii. p. 277 (1912).

electrons. This assumption seems to be legitimate when we remember that the mass and energy of the  $\alpha$  particle are very large compared with that of an electron even moving with a velocity comparable with that of light. Simple considerations show that the deflexions which an  $\alpha$  particle would experience even in passing through the complex electronic distribution of a heavy atom like gold, must be small compared with the large deflexions actually observed. In fact, the passage of swift  $\alpha$  particles through matter affords the most definite and straightforward method of throwing light on the gross structure of the atom, for the  $\alpha$  particle is able to penetrate the atom without serious disturbance from the electronic distribution, and thus is only affected by the intense field associated with the nucleus of the atom.

This independence of the large angle scattering on the external distribution of electrons is only true for charged particles whose kinetic energy is very large. It is not to be expected that it will hold for particles moving at very much lower speeds and with much less energy—such, for example, as the ordinary cathode particles or the recoil atoms from active matter. In such cases it is probable that the external electronic distribution plays a far more prominent part in governing the scattering than in the case under consideration.

#### *Scattering of $\beta$ particles.*

It is to be anticipated on the nucleus theory that swift  $\beta$  particles should suffer deflexions through large angles in their passage close to the nucleus. There seems to be no doubt that such large deflexions are actually produced, and I showed in my previous paper that the results of scattering of  $\beta$  particles found by Crowther\* could be generally explained on the nucleus theory of atomic structure. It should be borne in mind, however, that there are several important points of distinction between the effects to be expected for an  $\alpha$  particle and a  $\beta$  particle. Since the force between the nucleus and  $\beta$  particle is attractive, the  $\beta$  particle increases rapidly in speed in approaching the nucleus. On the ordinary electrodynamics, this entails a loss of energy by radiation, and also an increase of the apparent mass of the electron. Darwin† has worked out mathematically the result of these effects on the orbit of the electron, and has shown that, under certain conditions, the  $\beta$  particle does not escape from the atom but describes a spiral orbit ultimately

\* Crowther, Proc. Roy. Soc. A. lxxxiv. p. 226 (1910).

† Darwin, Phil. Mag. xxv. p. 201 (1913).

falling into the nucleus. This result is of great interest, for it may offer an explanation of the disappearance of swift  $\beta$  particles in their passage through matter. In addition, it must be borne in mind that the swiftest  $\beta$  particle expelled from radium C possesses only about one-third of the energy of the corresponding  $\alpha$  particle, while the average energy of the  $\beta$  particle is less than one-sixth of that of the  $\alpha$  particle. It is thus to be anticipated that the large angle scattering of a  $\beta$  particle by the nucleus will take place in regions where the  $\alpha$  particle will only suffer a small deflexion—regions for which the application of the simple theory may not have been accurately tested. For these reasons, it is of great importance to determine the laws of large angle scattering of  $\beta$  particles of different speeds in passing through matter, as it should throw light on a number of important points connected with atomic structure. Experiments are at present in progress in the laboratory to examine the scattering of such swift  $\beta$  particles in detail.

It is obvious that a  $\beta$  particle in passing close to an electron will occasionally suffer a large deflexion. The problem is mathematically similar to that for a close encounter of an  $\alpha$  particle with a helium atom of the same mass, which is discussed by Mr. Darwin in the accompanying paper. Such large deflexions due to electronic encounter, however, should be relatively small in number compared with those due to the nucleus of a heavy atom.

#### *Scattering in Hydrogen.*

Special interest attaches to the effects to be expected when  $\alpha$  particles pass through light gases like hydrogen and helium. In a previous paper by Mr. Nuttall and the author\*, it has been shown that the scattering of  $\alpha$  particles in hydrogen and helium is in good agreement with the view that the hydrogen nucleus has one positive charge, while the  $\alpha$  particle, or helium, has two. Mr. Darwin has worked out in detail the simple scattering to be anticipated when  $\alpha$  particles pass through hydrogen and helium. It is only necessary here to refer to the fact that on the nucleus theory a small number of hydrogen atoms should acquire, as the result of close encounters with  $\alpha$  particles, velocities about 1.6 times that of the velocity of the  $\alpha$  particle itself. On account of the fact that the hydrogen atom carries one positive charge while the  $\alpha$  particle carries two, it can be calculated that some of the hydrogen atoms should have a range in hydrogen of nearly four times that of the  $\alpha$  particle which sets them in motion.

\* Rutherford and Nuttall, *Phil. Mag.* xxvi. p. 702 (1913).



Mr. Marsden has kindly made experiments for me to test whether the presence of such hydrogen atoms can be detected. A detailed account of his experiments will appear later, but it suffices to mention here that undoubted evidence has been obtained by him that some of the hydrogen atoms are set in such swift motion that they are able to produce a visible scintillation on a zinc sulphide screen and are able to travel through hydrogen a distance three or four times greater than the colliding  $\alpha$  particle. The general method employed was to place a thin  $\alpha$ -ray tube containing about 100 millicuries of purified emanation in a tube filled with hydrogen. The scintillations due to the  $\alpha$  particle from the tube disappeared in air after traversing a distance of about 5 cm. When the air was displaced by hydrogen, the great majority of the scintillations disappeared at about 20 cm. from the source, which corresponds to the range of the  $\alpha$  particle in hydrogen. A small number of scintillations, however, persisted in hydrogen up to a distance of about 90 cm. The scintillations were of less intensity than those due to the ordinary  $\alpha$  particle. The number of scintillations observed is of the order of magnitude to be anticipated on the theory of single scattering, supposing that the nucleus in hydrogen and helium has such small dimensions, and that they behave like point charges for distances up to  $10^{-13}$  cm.

There appears to be no doubt that the scintillations observed beyond 20 cm. are due to charged hydrogen atoms which are set in swift motion by a close encounter with an  $\alpha$  particle. Experiments are at present in progress by Mr. Marsden to determine the number of hydrogen atoms set in motion, and the variation of the number with the scattering angle.

It does not appear possible to explain the appearance of such swift hydrogen atoms unless it be supposed that the forces of repulsion between the  $\alpha$  particle and the hydrogen atom are exceedingly intense. Such intense forces can only arise if the positive nuclei have exceedingly small dimensions, so that a close approach between them is possible.

#### *Dimensions and Constitution of the Nucleus.*

In my previous paper I showed that the nucleus must have exceedingly small dimensions, and calculated that in the case of gold its radius was not greater than  $3 \times 10^{-12}$  cm. In order to account for the velocity given to hydrogen atoms by the collision with  $\alpha$  particles, it can be simply calculated (see Darwin) that the centres of nuclei of helium and hydrogen must approach within a distance of  $1.7 \times 10^{-13}$  cm. of each other. Supposing for simplicity the nuclei to have dimensions



and to be spherical in shape, it is clear that the sum of the radii of the hydrogen and helium nuclei is not greater than  $1.7 \times 10^{-13}$  cm. This is an exceedingly small quantity, even *smaller* than the ordinarily accepted value of the diameter of the electron, viz.  $2 \times 10^{-13}$  cm. It is obvious that the method we have considered gives a maximum estimate of the dimensions of the nuclei, and it is not improbable that the hydrogen nucleus itself may have still smaller dimensions. This raises the question whether the hydrogen nucleus is so small that its mass may be accounted for in the same way as the mass of the negative electron.

It is well known from the experiments of Sir J. J. Thomson and others, that no positively charged carrier has been observed of mass less than that of the hydrogen atom. The exceedingly small dimensions found for the hydrogen nucleus add weight to the suggestion that the hydrogen nucleus is the *positive electron*, and that its mass is entirely electromagnetic in origin. According to the electromagnetic theory, the electrical mass of a charged body, supposed spherical, is  $\frac{2}{3} \frac{e^2}{a}$  where  $e$  is the charge and  $a$  the radius.

The hydrogen nucleus consequently must have a radius about  $1/1830$  of the electron if its mass is to be explained in this way. There is no experimental evidence at present contrary to such an assumption.

The helium nucleus has a mass nearly four times that of hydrogen. If one supposes that the positive electron, *i. e.* the hydrogen atom, is a unit of which all atoms are composed, it is to be anticipated that the helium atom contains four positive electrons and two negative.

It is well known that a helium atom is expelled in many cases in the transformation of radioactive matter, but no evidence has so far been obtained of the expulsion of a hydrogen atom. In conjunction with Mr. Robinson, I have examined whether any other charged atoms are expelled from radioactive matter except helium atoms, and the recoil atoms which accompany the expulsion of  $\alpha$  particles. The examination showed that if such particles are expelled, their number is certainly less than 1 in 10,000 of the number of helium atoms. It thus follows that the helium nucleus is a very stable configuration which survives the intense disturbances resulting in its expulsion with high velocity from the radioactive atom, and is one of the units, of which possibly the great majority of the atoms are composed. The radioactive evidence indicates that the atomic weight of successive products decreases by four units consequent on the expulsion of

an  $\alpha$  particle, and it has often been pointed out that the atomic weights of many of the permanent atoms differ by about four units.

It will be seen later that the resultant positive charge on the nucleus determines the main physical and chemical properties of the atom. The mass of the atom is, however, dependent on the number and arrangement of the positive and negative electrons constituting the atom. Since the experimental evidence indicates that the nucleus has very small dimensions, the constituent positive and negative electrons must be very closely packed together. As Lorentz has pointed out, the electrical mass of a system of charged particles, if close together, will depend not only on the number of these particles, but on the way their fields interact. For the dimensions of the positive and negative electrons considered, the packing must be very close in order to produce an appreciable alteration in the mass due to this cause. This may, for example, be the explanation of the fact that the helium atom has not quite four times the mass of the hydrogen atom. Until, however, the nucleus theory has been more definitely tested, it would appear premature to discuss the possible structure of the nucleus itself. The general theory would indicate that the nucleus of a heavy atom is an exceedingly complicated system, although its dimensions are very minute.

An important question arises whether the atomic nuclei, which all carry a positive charge, contain negative electrons. This question has been discussed by Bohr \*, who concluded from the radioactive evidence that the high speed  $\beta$  particles have their origin in the nucleus. The general radioactive evidence certainly supports such a conclusion. It is well known that the radioactive transformations which are accompanied by the expulsion of high speed  $\beta$  particles are, like the  $\alpha$  ray changes, unaffected by wide ranges of temperature or by physical and chemical conditions. On the nucleus theory, there can be no doubt that the  $\alpha$  particle has its origin in the nucleus and gains a great part, if not all, of its energy of motion in escaping from the atom. It seems reasonable, therefore, to suppose that a  $\beta$  ray transformation also originates from the expulsion of a negative electron from the nucleus. It is well known that the energy expelled in the form of  $\beta$  and  $\gamma$  rays during the transformation of radium C† is about one-quarter of the energy of the expelled  $\alpha$  particle. It does not seem easy to explain this large

\* Bohr, Phil. Mag. xxvi. p. 476 (1913).

† See Rutherford and Robinson, Phil. Mag. xxv. p. 301 (1913).

emission of energy by supposing it to have its origin in the electronic distribution. It seems more likely that a very high speed electron is liberated from the nucleus, and in its escape from the atom sets the electronic distribution in violent vibration, giving rise to intense  $\gamma$  rays and also to secondary  $\beta$  particles. The general evidence certainly indicates that many of the high speed electrons from radioactive matter are liberated from the electronic distribution in consequence of the disturbance due to the primary electron escaping from the nucleus.

*Charge on the Nucleus.*

We have seen that from an examination of the scattering of  $\alpha$  particles by matter, it has been found that the positive charge on the nucleus is approximately equal to  $\frac{1}{2}Ae$ , when  $A$  is the atomic weight and  $e$  the unit charge. This is equivalent to the statement that the number of electrons in the external distribution is about half the atomic weight in terms of hydrogen. It is of interest to note that this is the value deduced by Barkla \* from entirely different evidence, viz. the scattering of X rays in their passage through matter. This is founded on the theory of scattering given by Sir J. J. Thomson, which supposes that each electron in an atom scatters as an independent unit. It seems improbable that the electrons within the nucleus would contribute to this scattering, for they are packed together with positive nuclei and must be held in equilibrium by forces of a different order of magnitude from those which bind the external electrons.

It is obvious from the consideration of the cases of hydrogen and helium, where hydrogen has one electron and helium two, that the number of electrons cannot be exactly half the atomic weight in all cases. This has led to an interesting suggestion by van den Broek† that the number of units of charge on the nucleus, and consequently the number of external electrons, may be equal to the number of the elements when arranged in order of increasing atomic weight. On this view, the nucleus charges of hydrogen, helium, and carbon are 1, 2, 6 respectively, and so on for the other elements, provided there is no gap due to a missing element. This view has been taken by Bohr in his theory of the constitution of simple atoms and molecules.

Recently strong evidence of two distinct kinds has been

\* Barkla, Phil. Mag. xxi. p. 648 (1911).

† van den Broek, *Phys. Zeit.* xiv. p. 32 (1913).



brought in support of such a contention. Soddy\* has pointed out that the recent generalisation of the relation between the chemical properties of the elements and the radiations can be interpreted by supposing that the atom loses two positive charges by the expulsion of an  $\alpha$  particle, and one negative by the expulsion of a high speed electron. From a consideration of the series of products of the three main radioactive branches of uranium, thorium, and actinium, it follows that some of the radioactive elements may be arranged so that the nucleus charge decreases by one unit as we pass from one element to another. It would thus appear that van den Broek's suggestion probably holds for some if not all of the heavy radioactive elements. Recently Moseley† has supplied very valuable evidence that this rule also holds for a number of the lighter elements. By examination of the wave-length of the characteristic X rays emitted by twelve elements varying in atomic weight between calcium (40) and zinc (65.4), he has shown that the variation of wave-length can be simply explained by supposing that the charge on the nucleus increases from element to element by exactly one unit. This holds true for cobalt and nickel, although it has long been known that they occupy an anomalous relative position in the periodic classification of the elements according to atomic weights.

There appears to be no reason why this new and powerful method of analysis, depending on an examination of the frequency of the characteristic X ray spectra of the elements, should not be extended to a large number of elements, so that further definite data on the point may be expected in the near future.

It is clear on the nucleus theory that the physical and chemical properties of the ordinary elements are for the most part dependent entirely on the charge of the nucleus, for the latter determines the number and distribution of the external electrons on which the chemical and physical properties must mainly depend. As Bohr has pointed out, the properties of gravitation and radioactivity, which are entirely uninfluenced by chemical or physical agencies, must be ascribed mainly if not entirely to the nucleus, while the ordinary physical and chemical properties are determined by the number and distribution of the external electrons. On this view, the nucleus charge is a fundamental constant of the atom, while the atomic mass of an atom may be a complicated function of the arrangement of the units which make up the nucleus.

\* Soddy, *Jahr. d. Rad.* x. p. 188 (1913).

† Moseley, *Phil. Mag.* xxvi. p. 1024 (1913).



It should be borne in mind that there is no inherent impossibility on the nucleus theory that atoms may differ considerably in atomic weight and yet have the same nucleus charge. This is most simply illustrated by radioactive evidence. In the following table the atomic weight and nucleus charge are given for a few of the successive elements arising from the transformation of uranium. The actual nucleus charge of uranium is unknown, but for simplicity it is assumed to be 100.

Successive Elements	..	Ur <sub>1</sub>	→	Ur X <sub>1</sub>	→	Ur X <sub>2</sub>	→	Ur <sub>2</sub>	→	Io	→	Ra
Atomic weights	.....	238.5		234.5		234.5		234.5		230.5		226.5
Charge on nucleus	....	100		98		99		100		98		96

Following the recent theories, it is supposed that the emission of an  $\alpha$  particle lowers the nucleus charge by two units, while the emission of a  $\beta$  particle raises it by one unit. It is seen that Ur<sub>1</sub> and Ur<sub>2</sub> have the same nucleus charge although they differ in atomic weight by four units.

If the nucleus is supposed to be composed of a mixture of hydrogen nuclei with one charge and of helium nuclei with two charges, it is *a priori* conceivable that a number of atoms may exist with the same nucleus charge but of different atomic masses. The radioactive evidence certainly supports such a view, but probably only a few of such possible atoms would be stable enough to survive for a measurable time.

Bohr \* has drawn attention to the difficulties of constructing atoms on the "nucleus" theory, and has shown that the stable positions of the external electrons cannot be deduced from the classical mechanics. By the introduction of a conception connected with Planck's quantum, he has shown that on certain assumptions it is possible to construct simple atoms and molecules out of positive and negative nuclei, *e. g.* the hydrogen atom and molecule and the helium atom, which behave in many respects like the actual atoms or molecules. While there may be much difference of opinion as to the validity and of the underlying physical meaning of the assumptions made by Bohr, there can be no doubt that the theories of Bohr are of great interest and importance to all physicists as the first definite attempt to construct simple atoms and molecules and to explain their spectra.

University of Manchester,  
February 1914.

\* Bohr, Phil. Mag. xxvi. pp. 476, 857 (1913).

LVIII. *Collision of  $\alpha$  Particles with Light Atoms.* By C. G. DARWIN, M.A., *Reader in Mathematical Physics, University of Manchester* \*.

1. **I**N order to account for the fact that  $\alpha$  particles are sometimes deflected through large angles, Rutherford † put forward the hypothesis that the positive electricity in an atom carries its mass and is concentrated in an excessively small region. The experiments of Geiger and Marsden ‡ fully confirmed this theory, and they succeeded in calculating the nuclear charge for a few substances. They found it to be about half the atomic weight multiplied by the electronic charge. Rutherford's calculations apply to the case where an  $\alpha$  particle collides with a heavy atom, and, for simplicity, he assumes that the collision does not set the atom in motion. His work requires modification to include the fact that the nucleus of the atom is set in motion, and it is this question that is treated in the present paper.

2. We first require the result of a single collision. In finding this we may neglect the effects of the electrons in the atom on account of their small mass. Let  $EM$  be the charge and mass of the  $\alpha$  particle,  $em$  of the nucleus. Let  $V$  be the initial velocity of the  $\alpha$  particle. The nucleus starts from rest. There are four unknown quantities to be determined by the collision, the velocity  $v$  and deflexion  $\phi$  of the  $\alpha$  particle, and the velocity  $u$  and direction of motion of the nucleus. The latter is in the plane determined by the initial and final motions of the  $\alpha$  particle. Let it be at angle  $\theta$  from the initial direction. For convenience  $\theta$  is measured in the opposite direction from  $\phi$ . When one of these quantities is known the other three can be determined by the principles of momentum and energy. To find the frequency of a given set of values of  $v$  &c. we must calculate the orbits.

The equations of momentum and energy are :—

$$\left. \begin{aligned} MV &= Mv \cos \phi + mu \cos \theta, \\ 0 &= Mv \sin \phi - mu \sin \theta, \\ MV^2 &= Mv^2 + mu^2. \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad (1)$$

\* Communicated by Sir Ernest Rutherford, F.R.S.

† Rutherford, *Phil. Mag.* vol. xxi. p. 669 (1911).

‡ Geiger and Marsden, *Phil. Mag.*

From these we derive :—

$$\left. \begin{aligned} u &= 2V \frac{M}{M+m} \cos \theta, \\ \tan \phi &= \frac{m \sin 2\theta}{M-m \cos 2\theta}, \end{aligned} \right\} \dots \dots \dots (2)$$

and

$$\left. \begin{aligned} v &= \frac{V}{M+m} \{M \cos \phi \pm \sqrt{(m^2 - M^2 \sin^2 \phi)}\}, \\ \tan \theta &= \frac{m \cot \phi \pm \sqrt{(m^2 \operatorname{cosec}^2 \phi - M^2)}}{M+m}, \end{aligned} \right\} \dots (3)$$

For the present we shall leave the ambiguities undetermined ; but the two upper and the two lower signs go together.

To find the frequency for a collision of this type we must use the orbit. Now, in the case where the nucleus is heavy, Rutherford \* showed that when the  $\alpha$  particle approaches along a line at distance  $p$  from the nucleus, the deflexion is  $2\mu$  where

$$\tan \mu = \frac{eE}{pV^2} \frac{1}{M}.$$

The apsidal distance is

$$p \tan \left( \frac{\pi}{4} - \frac{\mu}{2} \right).$$

By a well-known process in the theory of orbits, this can be adapted to the more general case by replacing  $1/M$  by  $1/M + 1/m$ . The result then applies to the *relative* orbit of the  $\alpha$  particle.

Thus if

$$\tan \mu = \frac{eE}{pV^2} \left( \frac{1}{M} + \frac{1}{m} \right),$$

the relative deflexion is  $2\mu$ , and so

$$\tan 2\mu = \frac{v \sin \phi + u \sin \theta}{v \cos \phi - u \cos \theta},$$

which, by use of (1) and (2), can be reduced to  $-\tan 2\theta$ .

Hence  $\theta = \frac{\pi}{2} - \mu$ .

Thus

$$p = \tan \theta \frac{eE}{V^2} \left( \frac{1}{M} + \frac{1}{m} \right) \dots \dots \dots (4)$$

and the apsidal distance is

$$\frac{eE}{V^2} \left( \frac{1}{M} + \frac{1}{m} \right) (1 + \sec \theta) \dots \dots \dots (5)$$

\* Rutherford, *loc. cit.*

Let  $N$  be the number of atoms per c.c. Let  $Q \propto$  particles pass in each second through a foil of thickness  $t$ . Then  $Qt N 2\pi p dp$  of them pass within a distance between  $p$  and  $p + dp$  from some nucleus; and all these undergo a deflexion  $\phi$ . Suppose that  $\nu$  are observed per second within a solid angle  $\omega$  at inclination  $\phi$ . Then

$$\nu = QtN\omega \frac{p dp}{\sin \phi d\phi}.$$

If we substitute the value of  $p$  in terms of  $\phi$  deduced from (4) and (3) we get the accurate formula for  $\nu$ , viz. :—

$$\nu = QtN\omega \frac{1}{V^4} \frac{e^2 E^2}{M^2} \operatorname{cosec}^3 \phi \frac{\left[ \cot \phi \pm \sqrt{\operatorname{cosec}^2 \phi - \left(\frac{M}{m}\right)^2} \right]^2}{\sqrt{\left(\operatorname{cosec}^2 \phi - \left(\frac{M}{m}\right)^2\right)}}. \quad (6)$$

3. We must now remove the ambiguity of sign. This depends on the values of  $M$  and  $m$ .

*Case I.  $m > M$ .* This will refer to all substances except hydrogen and helium. Consideration of the special cases  $\phi = 0$  and  $\phi = \pi$  shows that the upper sign is to be taken.

If the expression is expanded in powers of  $\frac{M}{m}$  we find

$$\nu = QtN\omega \frac{1}{V^4} \frac{e^2 E^2}{M^2} \frac{1}{4} \left\{ \operatorname{cosec}^4 \frac{\phi}{2} - 2 \left(\frac{M}{m}\right)^2 + \left(1 - \frac{3}{2} \sin^2 \phi\right) \left(\frac{M}{m}\right)^4 + \dots \right\}.$$

The first term of the expansion is that given by Rutherford.

Since  $\operatorname{cosec}^4 \frac{\phi}{2}$  is always greater than 1, the result is correct to 1 per cent. with these three terms, even when  $\frac{M}{m}$  is as

high as  $\frac{1}{3}$ , the value it would have for carbon. From (2) we see that the velocity of the carbon nucleus may rise as high as  $\frac{1}{2}V$ . Such a particle might possibly be perceptible, but it is doubtful whether the shock would free the nucleus of all its electrons, and the experimental conditions to reveal it are rather hard to imagine.

*Case II.  $m = M$ .* The  $\alpha$  particle now travels through helium. We have still to take the positive sign in the ambiguities. Then we get :—

$$v = V \cos \phi, \quad u = V \cos \theta, \quad \phi = \frac{\pi}{2} - \theta.$$

The  $\alpha$  particle and nucleus diverge from one another at



right angles, and no particle can be deflected through more than a right angle.

$$\nu = Q t N \omega \frac{1}{V^4} \frac{e^2 E^2}{M^2} 4 \cot \phi \operatorname{cosec}^3 \phi.$$

But to this number we must add the helium atoms which have been set in motion so as to strike the screen. They number

$$Q t N \omega \frac{p dp}{\sin \theta d\theta} = Q t N \omega \frac{1}{V^4} \frac{e^2 E^2}{M^2} 4 \sec^3 \theta.$$

Since the energy of ionization is negligible they have velocity  $V \cos \theta$ .

To find the whole number on the screen we replace  $\theta$  by  $\phi$  and get

$$\nu = Q t N \omega \frac{1}{V^4} \frac{e^2 E^2}{M^2} 4 \cos \phi \operatorname{cosec}^4 \phi (1 + \tan^4 \phi).$$

The recoiling particles should be quite indistinguishable from true  $\alpha$  particles. Indeed there is a reciprocal relation. If an  $\alpha$  particle goes in a direction  $\phi$  with velocity  $v$  while simultaneously the nucleus goes in direction  $\theta$  with velocity  $u$ , then it is possible for an  $\alpha$  particle to go to  $\theta$  with velocity  $u$  while the nucleus goes to  $\phi$  with velocity  $v$ .

*Case III.*  $m < M$ . The  $\alpha$  particles pass through hydrogen. We have actually  $m = \frac{1}{4}M$ , and this special case is the only one that need be studied.

$m^2 - M^2 \sin^2 \phi$  becomes negative if  $\phi > 14^\circ 29'$ . Thus no  $\alpha$  particles are deflected through angles greater than this. For less angles there are two types of  $\alpha$  particles determined by the two signs of the ambiguity. For example, in the undeflected direction there are  $\alpha$  particles which have not been in collision at all, and also those which have struck a nucleus perfectly straight and have then followed on. Thus, in general, at any angle  $\phi$  there are  $\alpha$  particles of two velocities:

$$v = V \frac{1}{3} [4 \cos \phi + \sqrt{1 - 16 \sin^2 \phi}]$$

and

$$v = V \frac{1}{3} [4 \cos \phi - \sqrt{1 - 16 \sin^2 \phi}],$$

and to each corresponds a different value of  $\theta$  which is given by the two signs in (3).

Thus

$$\nu = Q t N \omega \frac{1}{V^4} \frac{e^2 E^2}{M^2} \operatorname{cosec}^3 \phi \frac{(\cot \phi + \sqrt{\operatorname{cosec}^2 \phi - 16})^2 + (\cot \phi - \sqrt{\operatorname{cosec}^2 \phi - 16})^2}{\sqrt{(\operatorname{cosec}^2 \phi - 16)}}$$

This formula becomes infinite in the neighbourhood of  $\phi = 14^\circ 29'$ . In fact, there will be a considerable increase in the number of scintillations near this angle, since a large change in  $p$  makes little difference in the deflexion. A finite formula can be obtained by expressing the whole number deflected through angles greater than any given angle. Near the limiting angle the field of the microscope, however small, will cease to be uniform.

To the above number  $\nu$  must be added the effects of the recoiling H particles. Their number is

$$QNt\omega \frac{p dp}{\sin \theta d\theta} = QNt\omega \frac{1}{V^4} \frac{e^2 E^2}{M^2} 25 \sec^3 \theta.$$

The whole number of scintillations observed is thus

$$QNt\omega \frac{1}{V^4} \frac{e^2 E^2}{M^2} \left\{ \operatorname{cosec}^3 \phi \frac{2 \operatorname{cosec}^2 \phi - 17}{\sqrt{(\operatorname{cosec}^2 \phi - 16)}} + 25 \sec^3 \phi \right\}.$$

They are of three types, slow  $\alpha$  particles, fast  $\alpha$  particles, and H particles. Since  $u = V \frac{5}{3} \cos \theta$ , the last are very much faster than either of the first.

4. It is of great interest to see how these H particles may be expected to behave. In passing through matter they will be retarded like  $\alpha$  particles, and we may calculate their range. To do this we take Bohr's formula \*

$$\frac{dV}{dv} = -4\pi \frac{e'^2 E^2 N}{m' M V^3} \sum \log \frac{V^3 k M m'}{n_s e' E (M + m')}.$$

Here  $N$  is the number of atoms per c.c.,  $e' m'$  refer to an electron,  $k$  is a numerical constant, and  $n_s$  the natural frequency of any of the electrons in the atom. For a H particle  $E$  is to be halved and  $M$  quartered. The result thus does not affect the factor outside the sum, while inside we have to add a term  $r \log 2$ , where  $r$  is the number of electrons in the atom. Thus the range of a H particle will be slightly less than that of an  $\alpha$  particle of the same initial velocity. The most important case is where the H particles are travelling through hydrogen. For this Bohr takes  $r=1$  and so we have

$$\frac{dV}{dv} = -\frac{A}{V^3} (\log BV^3 + \log 2)$$

instead of

$$\frac{dV}{dv} = -\frac{A}{V^3} \log BV^3.$$

\* Bohr, Phil. Mag. vol. xxv. p. 10 (1913).

Bohr's theory does not supply a definite value for the range, as his approximation ceases to hold for low velocities. We can get an estimate by adopting Geiger's empirical formula

$$V^3 = V_0^3 \left(1 - \frac{x}{R}\right)$$

and making  $\frac{dV}{dx}$  have the proper initial value. Since

$$\left(\frac{dV}{dx}\right)_0 = -\frac{1}{3} \frac{V_0}{R}$$

we have

$$\frac{1}{3} \frac{V_0}{R} = \frac{A}{V_0^3} \log BV_0^3, \quad \text{and} \quad \frac{1}{3} \frac{V_0}{R'} = \frac{A}{V_0^3} (\log BV_0^3 + \log 2),$$

where the accent refers to the H particle.

Taking  $V_0 = 2 \times 10^9$  cm. per sec.,  $A = 2.4 \times 10^{34}$  and  $R = 31$  cm. we deduce  $R' = 28$  cm. For heavier substances higher multiples of  $\log 2$  will occur and the range will be relatively less. Now consider a collision of the most favourable type possible, when an  $\alpha$  particle at its highest velocity strikes a nucleus straight on. If the  $\alpha$  particle is from RaC the initial velocity of the H particle is  $\frac{8}{5} \times 2 \times 10^9$  cm. per sec., and its range is therefore  $28 \times \left(\frac{8}{5}\right)^3$  cm. or 117 cm. It should probably be more than

this, as for these high speeds the range should be more nearly proportional to the fourth than to the third power of the velocity. Thus the H particles ought to be easily observable provided they can be made to occur in sufficient numbers.

The H particles should be more scattered than  $\alpha$  particles by their atomic encounters, for the angle of most probable scattering depends on  $\frac{E}{M}^*$ , and so is twice as great for H as for  $\alpha$  particles.

5. The experiments of Geiger and Marsden confirmed very completely the nuclear hypothesis, but it might be argued that some other law of force might give the same result. It might be difficult to give a general proof that this is not so, but we can show that no force proportional to some power of the distance other than the inverse square can give the observed dependence of  $\nu$  on  $V$ . If the force is as the inverse

\* Darwin, Phil. Mag. vol. xxiii. p. 907 (1912).

cube of the distance, we can also work out the orbits and show that the dependence of  $\nu$  on angle disagrees with experiment. For simplicity we shall suppose the nucleus immovable. In polar coordinates the motion is given by:—

$$r^2\dot{\theta} = pV \text{ and } \dot{r}^2 + r^2\dot{\theta}^2 = V^2 - \frac{\mu}{r^{n-1}},$$

where the force is proportional to  $\frac{1}{r^n}$ .

If  $\frac{p}{r} = u$  we have

$$\left(\frac{du}{d\theta}\right)^2 + u^2 = 1 - \frac{\mu}{p^{n-1}V^2}u^{n-1}.$$

The deflexion  $\phi$  must therefore be a function of  $p^{n-1}V^2$  or inverting  $p = V^{-\frac{2}{n-1}}f(\phi)$ . The number of scintillations seen on a screen is proportional to  $\frac{p dp}{\sin \phi d\phi}$ , and, as far as it concerns the velocity, this is proportional to  $V^{-\frac{4}{n-1}}$ . Thus only if  $n=2$  can  $\nu$  be proportional to  $\frac{1}{V^4}$ .

When  $n=3$  the orbit can be worked out completely and we find

$$\phi = \pi - \frac{\pi}{\sqrt{\left(1 + \frac{\mu}{p^2V^2}\right)}},$$

from which we derive that  $\nu$  is proportional to

$$\frac{1}{V^2} \operatorname{cosec} \phi \frac{\left(1 - \frac{\phi}{\pi}\right)}{\left[\frac{\phi}{\pi}\left(2 - \frac{\phi}{\pi}\right)\right]^2}.$$

The ratio of the numbers at  $30^\circ$  and  $150^\circ$  for this law is 51. For the inverse square law it is 194. For a comparison of  $10^\circ$  and  $90^\circ$  the inverse cube gives 525 and the inverse square 4330.

6. We may calculate an upper limit to the size of atomic nuclei from the distance of closest approach between the  $\alpha$  particle and nucleus. By (5) the apsidal distance is

$$\frac{eE}{V^2} \left( \frac{1}{M} + \frac{1}{m} \right) (1 + \sec \theta),$$

and for any fairly strong deflexion of the  $\alpha$  particle  $\sec \theta$  is practically 1, so that we may take the distance as

$$2 \frac{eE}{V^2} \left( \frac{1}{M} + \frac{1}{m} \right).$$



For gold the number of deflexions was observed up to  $\phi=150^\circ$  and found to be correct. Taking  $e$  as 100 times the electronic charge and  $V=2 \times 10^9$  cm. per sec., this gives as the closest approach of nucleus and  $\alpha$  particle  $3.5 \times 10^{-12}$  cm.

The closest possible approach of all is between an  $\alpha$  particle and a hydrogen nucleus in a straight-on collision. With  $V=2 \times 10^9$  this gives a distance  $1.7 \times 10^{-13}$  cm. If it can be verified that the distribution of H particles is as predicted in this paper, then we may conclude that the radii of the nuclei of hydrogen and helium are certainly less than  $10^{-13}$  cm.

LIX. *On the Effect of Electric and Magnetic Fields on Spectral Lines.* By N. BOHR, Dr.phil. Copenhagen\*.

IN a previous paper† the writer has shown that an explanation of some of the laws of line spectra may be obtained by applying Planck's theory of black radiation to Rutherford's theory of the structure of atoms. In the present paper these considerations will be further developed, and it will be shown that it seems possible on the theory to account for some of the characteristic features of the recent discovery by Stark‡ of the effect of an electric field on spectral lines, as well as of the effect of a magnetic field first discovered by Zeeman. It will also be shown that the theory seems to offer an explanation of the appearance of ordinary double spectral lines§.

§ 1. *The Emission of a Line Spectrum.*

The theory put forward by the writer to explain the emission of a line-spectrum may be summarized as follows:—

The principal assumption of Planck's theory is that the

\* Communicated by Sir E. Rutherford, F.R.S.

† Phil. Mag. vol. xxvi. pp. 1, 476, 857 (1913).

‡ *Sitzungsb. d. Kgl. Akad. d. Wiss. Berlin*, 1913, p. 932.

§ While this paper was in course of preparation, a theoretical paper dealing with the same subject was published by E. Warburg (*Verh. d. deutsch. Phys. Ges.* xv. p. 1259 (1913)). The latter finds that the effect of electric and magnetic fields to be expected on my theory of the hydrogen spectrum is of the same order of magnitude as determined by experiment. However, contrary to the conclusions of the present paper, Warburg concludes that it does not seem possible on the theory to account in detail for the experimental results. In his opinion the theory leads to a broadening of the hydrogen lines in an electric field, instead of the appearance of the homogeneous components observed by Stark. He also calculates that the Zeeman effect should vary from line to line in a manner inconsistent with experiment.

energy of a system of vibrating electrified particles cannot be transferred into radiation, and *vice versa*, in the continuous way assumed in the ordinary electrodynamics, but only in finite quanta of the amount  $h\nu$ , where  $h$  is a universal constant and  $\nu$  the frequency of the radiation \*. Applying this assumption to the emission of a line-spectrum, and assuming that a certain spectral line of frequency  $\nu$  corresponds to a radiation emitted during the transition of an elementary system from a state in which its energy is  $A_1$  to one in which it is  $A_2$ , we have

$$h\nu = A_1 - A_2. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

According to Balmer, Rydberg, and Ritz the frequency of the lines in the line-spectrum of an element can be expressed by the formula

$$\nu = f_r(n_1) - f_s(n_2), \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where  $n_1$  and  $n_2$  are whole numbers and  $f_1, f_2, \dots$  a series of functions of  $n$ , which can be expressed by

$$f_r(n) = \frac{K}{n^2} \phi_r(n), \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where  $K$  is a universal constant and  $\phi$  a function which for large values of  $n$  approaches the value unity. The complete spectrum is obtained by combining the numbers  $n_1$  and  $n_2$  as well as the functions  $f_1, f_2, \dots$ , in every possible way.

On the above view this can be interpreted by assuming :

(1) That every line in the spectrum corresponds to a radiation emitted by a certain elementary system during its passage between two states in which the energy, omitting an arbitrary constant, is given by  $-hf_s(n_2)$  and  $-hf_r(n_1)$  respectively ;

(2) That the system can pass between any two such states during emission of a homogeneous radiation.

The states in question will be denoted as "stationary states."

\* In Planck's original theory certain other assumptions about the properties of the vibrating systems were used. However, Debye (*Ann. d. Phys.* xxxiii. p. 1427 (1910)) has shown that it is possible to deduce Planck's formula of radiation without using any assumption about the vibrators, if it be supposed that energy can be transferred between them and the radiation, only in finite quanta  $h\nu$ . It may further be remarked that Poincaré (*Journ. d. Physique*, ii. p. 5 (1912)) has deduced the necessity of assuming that the transference of energy takes place in quanta  $h\nu$  in order to explain the experimental laws of black radiation.

The spectrum of hydrogen observed in ordinary vacuum-tubes \* is represented by (2) and (3) by putting

$$\phi_1(n) = \phi_2(n) = \dots = 1. \quad . \quad . \quad . \quad (4)$$

Accordingly we shall assume that this spectrum is emitted by a system possessing a series of stationary states in which, corresponding to the  $n$ th state, the energy, omitting the arbitrary constant, is given by

$$A_n = -h \frac{K}{n^2}. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

According to Rutherford's theory, the atom of an element consists of a central positive nucleus surrounded by electrons rotating in closed orbits. Concordant evidence, obtained in very different ways, indicates that the number of electrons in the neutral atom is equal to the number of the corresponding element in the periodic table †.

On this theory the structure of the neutral hydrogen atom is of extreme simplicity; it consists of an electron rotating round a positive nucleus of opposite charge. In such a system we get on the ordinary mechanics the following equations for the frequency of revolution  $\omega$  and the major axis  $2a$  of the relative orbit of the particles

$$\omega^2 = \frac{2W^3(M+m)}{\pi^2 e^4 m M}, \quad 2a = \frac{e^2}{W}. \quad . \quad . \quad . \quad (6)$$

where  $e$  and  $-e$  are the charges,  $M$  and  $m$  the masses of the nucleus and the electron respectively, and where  $W$  is the amount of energy to be transferred to the system in order to remove the electron to an infinite distance from the nucleus. It may be noticed that the expressions are independent of the degree of eccentricity of the orbits.

In order to obtain a mechanical interpretation of the above-mentioned stationary states, let us now in (6) put  $W_n = -A^*$ . This gives

$$W_n = \frac{hK}{n^2}, \quad \omega_n^2 = \frac{2h^3 K^3 (M+m)}{\pi^2 e^4 m M n^6}, \quad 2a_n = \frac{e^2 n^2}{hK}. \quad . \quad (7)$$

According to this view, a line of the hydrogen spectrum is emitted during the passage of the atom between two

\* A series of lines, first observed by Pickering in stellar spectra and recently by Fowler in vacuum-tubes containing a mixture of hydrogen and helium, is generally also ascribed to hydrogen. These lines, however, can be accounted for on the present theory, if we ascribe them to helium. (Phil. Mag. *loc. cit.* p. 10; comp. also 'Nature,' xcii. p. 231 (1913).)

† Comp. A. v. d. Broek, *Phys. Zeitschr.* xiv. p. 32 (1913), comp. also several recent contributions to 'Nature.'

stationary states corresponding to different values for  $n$ . We must assume that the mechanism of emission cannot be described in detail on the basis of the ordinary electrodynamics. However, it is known that it is possible on the latter theory to account satisfactorily for the phenomena of radiation in the region of slow vibrations. If our point of view is sound, we should therefore expect to find in this region some connexion between the present theory and the ordinary ideas of electrodynamics.

From (7) we see that  $\omega_n$  vanishes for large values of  $n$ , and that at the same time the ratio  $\omega_n/\omega_{n+1}$  tends to unity. On the present theory the frequency of the radiation emitted by the transition from the  $(n+1)$ th to the  $n$ th stationary state is equal to  $\frac{1}{h}(A_{n+1}-A_n)$ . When  $n$  is large, this

approaches to  $\frac{1}{h} \frac{dA_n}{dn}$ . On the ordinary electrodynamics we should expect the frequency of the radiation to be equal to the frequency of revolution, and consequently it is to be anticipated that for large values of  $n$

$$\frac{dA_n}{dn} = h\omega_n. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Introducing the values for  $A_n$  and  $\omega_n$  given by (5) and (7), we see that  $n$  disappears from this equation, and that the condition of identity is

$$K = \frac{2\pi^2 e^4 m M}{h^3 (M+m)}. \quad . \quad . \quad . \quad . \quad . \quad (9)$$

From direct observations we have  $K = 3.290 \cdot 10^{15}$ . Introducing recent values for  $e$ ,  $m$ , and  $h^*$ , we get for the expression on the right side of (9)  $3.26 \cdot 10^{15}$ . The agreement is inside the limit of experimental errors in the determination of  $e$ ,  $m$ , and  $h$ ; and we may therefore conclude that the connexion sought between the present considerations and the ordinary electrodynamics actually exists.

From (7) and (9) we get

$$W_n = \frac{2\pi^2 e^4 m M}{n^2 h^2 (M+m)}, \quad \omega_n = \frac{4\pi^2 e^4 m M}{n^3 h^3 (M+m)}, \quad 2a_n = \frac{n^2 h^2 (M+m)}{2\pi^2 e^2 m M}. \quad (10)$$

For  $n=1$ , corresponding to the normal state of the atom, we get  $2a = 1.1 \cdot 10^{-8}$ ; a value of the same order of magnitude as the values for the diameters of atoms calculated on

\* Phil. Mag. *loc. cit.* p. 487.



the kinetic theory of gases. For higher values of  $n$ , however,  $2a$  is great compared with the values of ordinary atomic dimensions. As I pointed out in my former paper, this result may be connected with the non-appearance in vacuum-tubes of hydrogen lines corresponding to high numbers in Balmer's formula and observed in the spectra of stars. Further, it will appear from the considerations of the next section that the large diameter of the orbits offers an explanation of the surprisingly great magnitude of the Stark effect.

From (10) it appears that the condition (8) holds, not only for large values of  $n$  but for all values of  $n$ . In addition, for a stationary orbit  $W$  is equal to the mean value of the total kinetic energy  $T$  of the particles; from (10) we therefore get

$$T_n = \frac{1}{2} n h \omega_n. \quad . \quad . \quad . \quad . \quad . \quad (11)$$

In using the expressions (6) we have assumed that the motion of the particles in the stationary states of the system can be determined by help of the ordinary mechanics. On this assumption it can be shown generally that the conditions (8) and (11) are equivalent. Consider a particle moving in a closed orbit in a stationary field. Let  $\omega$  be the frequency of revolution,  $T$  the mean value of the kinetic energy during a revolution, and  $-W$  the mean value of the sum of the kinetic energy and the potential energy of the particle relative to the stationary field. Applying Hamilton's principle, we get for a small variation of the orbit

$$\delta W = -2\omega \delta \left( \frac{T}{\omega} \right). \quad . \quad . \quad . \quad . \quad . \quad (12)$$

If the new orbit is also one of dynamical equilibrium, we get  $\delta A = -\delta W$ , where  $A$  is the total energy of the system, and it will be seen that the equivalence of (8) and (11) follows immediately from (12).

In these deductions we have made no assumptions about the degree of eccentricity of the orbits. If the orbits are circular (11) is equivalent to the simple condition that the angular momentum of the system in the stationary states is equal to an entire multiple of  $\frac{h}{2\pi}$ .\*

In Planck's vibrators the particles are held by quasi-elastic forces, and the mean value of the kinetic energy is

\* Comp. J. W. Nicholson, Month. Not. Roy. Astr. Soc. lxxii, p. 679 (1912).

equal to the mean value of the potential energy due to the displacements. Consequently (11) forms a complete analogy to Planck's original relation

$$U = nh\nu$$

between the energy  $U$  of a monochromatic vibrator and its frequency  $\nu$ . This analogy offers another way of representing the present theory—a way more similar to that used in my former paper\*. Considering, however, the widely different assumptions underlying the relation (11) and Planck's relation, it may seem more adequate not to seek the basis of our considerations in the formal analogy in question, but directly in the principal condition (1) and in the laws of the line-spectra.

In dealing with the more complicated structure of the spectra of other elements, we must assume that the atoms of such elements possess several different series of stationary states. This complexity of the system of stationary states, compared with that of the hydrogen atom, might naturally be anticipated from the greater number of electrons in the heavier atoms, which render possible several different types of configurations of the particles.

According to (1), (2), and (3) the energy of the  $n$ th state in the  $r$ th series is, omitting the arbitrary constant, given by

$$A_{n,r} = -\frac{hK}{n^2} \phi_r(n). \quad . \quad . \quad . \quad . \quad (13)$$

The present theory is not sufficiently developed to account in detail for the expression (13). However, a simple interpretation may be obtained of the fact that in every series  $\phi_r(n)$  approaches unity for large values of  $n$ .

Suppose that in the stationary states one of the electrons moves at a distance from the nucleus which is large compared with the distance of the other electrons. If the atom is neutral, the outer electron will be subject to very nearly the same forces as the electron in the hydrogen atom. Consequently, the expression (13) may be interpreted as indicating the presence of a number of series of stationary states of the

\* *Note added during the proof.*—In the *Phys. Zeitschr.* of Feb. 1, E. Gehrcke has attempted to represent the theory of the hydrogen spectrum in a way somewhat different from that in my former paper. Like the procedure in my paper, Gehrcke does not attempt to give a mechanical explanation of Planck's relation between the frequency of the radiation and the amount of energy emitted; but he does also not try to give a mechanical interpretation of the dynamical equilibrium of the atom in its possible stationary states, or to obtain a connexion to ordinary mechanics in the region of slow vibrations.

atom in which the configuration of the inner electrons is very nearly the same for all states in one series, while the configuration of the outer electron changes from state to state in the series approximately in the same way as in the hydrogen atom.

It will appear that these considerations offer a possible simple explanation of the appearance of the Rydberg constant in the formula for the spectral series of every element. In this connexion, however, it may be noticed that on this point of view the Rydberg constant is not exactly the same for every element, since the expression (8) for  $K$  depends on the mass of the central nucleus. The correction due to the finite value of  $M$  is very small for elements of high atomic weight, but is comparatively large for hydrogen. It may therefore not be permissible to calculate the Rydberg constant directly from the hydrogen spectrum. Instead of the value 109675 generally assumed, the theoretical value for a heavy atom is 109735.

## § 2. *The Effect of an Electric Field.*

As mentioned above, J. Stark has recently discovered that the presence of an external electric field produces a characteristic effect on the line-spectrum of an element. The effect was observed for hydrogen and helium. By spectroscopic observation in a direction perpendicular to the field, each of the lines of the hydrogen spectrum was broken up into five homogeneous components situated very nearly symmetrically with regard to the original line. The three inner components were of feeble intensity and polarized with electric vector perpendicular to the field, while the two outer stronger components were polarized with electric vector parallel to the field. The distance between the components was found to be proportional to the electric force within the limits of experimental errors. With a field of 13,000 volt per cm. the observed difference in the wave-length of the two outer components was  $3.6 \times 10^{-8}$  cm. and  $5.2 \times 10^{-8}$  cm. for  $H_\beta$  and  $H_\gamma$  respectively. For both systems of lines emitted by helium, Stark observed an effect on the lines of the Diffuse series which was of the same order of magnitude as that observed for the hydrogen lines, but of a different type. Thus the components were situated unsymmetrically with regard to the original line, and were also not polarized relative to the field. The effect of the field on the lines of the Principal series and the Sharp series was very small and hardly distinguishable.

On the theory of this paper the effect of an external field

on the lines of a spectrum may be due to two different causes:—

(1) The field may influence the stationary states of the emitting system, and thereby the energy possessed by the system in these states.

(2) It may influence the mechanism of transition between the stationary states, and thereby the relation between the frequency of the radiation and the amount of energy emitted.

Considering an external *electric* field we shall not expect an effect of the second kind. Having assumed the atoms to be systems of particles governed by electrostatic forces, we may consider the presence of the field simply as a complication of the original system; but on the interpretation given in the former section of the general principle of Ritz of combination of spectral lines, we may expect that the relation (1) will hold for every system of electrified particles.

It appears that a necessary condition for the correctness of this view is that the frequencies of the components of spectral lines produced by the electric field can be expressed by a formula of the type (2). As we shall see, this seems to be consistent with Stark's experiments.

Let us first consider the effect of an electric field on the hydrogen spectrum. In order to find the effect of the field on the energy of the atom in the different stationary states, we shall seek for its influence on the relation between the energy and the frequency of the system. In this calculation we shall make use of the ordinary mechanics, from analogy with the considerations of the former section.

For simplicity, let us suppose that the mass of the nucleus is infinitely great in comparison with that of the electron. Consider an electron originally moving in a circular orbit round the nucleus. Through the effect of an external electric field the orbit will be deformed. If the force is not accurately perpendicular to the plane of the orbit, this deformation will in course of time be considerable, even if the external electric force is very small compared with the attraction between the particles. In this case, the orbit may at every moment be considered as an ellipse with the nucleus in the focus, and the effect of the field will consist in a gradual variation of the direction of the major-axis as well as of the eccentricity. During this variation, the length of the major-axis will approximately remain constant and equal to the diameter of the original circular orbit. A detailed investigation of the motion of the electron may be



very complicated; but it can be simply shown that the problem only allows of two stationary orbits of the electron. In these, the eccentricity is equal to 1 and the major-axis parallel to the axis of the external field; the orbits simply consist of a straight line through the nucleus parallel to the axis of the field, one on each side of it. It can also be shown that orbits which are very near to these limiting cases will be very nearly stationary.

Neglecting quantities proportional to the square of the magnitude of the external electric force, we get for the rectilinear orbits in question

$$\omega^2 = \frac{e^2}{4\pi^2 ma^3} \left(1 \mp 3E \frac{a^2}{e}\right), \quad . \quad . \quad . \quad (14)$$

where  $\omega$  is the frequency of vibration and  $2a$  the amplitude of the orbit.  $E$  is the external electric force, and the two signs correspond to orbits in which the direction of the major-axis from the nucleus is the same or opposite to that of the electric force respectively. For the total energy of the system we have

$$A = C - \frac{e^2}{2a} \mp 2aeE, \quad . \quad . \quad . \quad . \quad (15)$$

where  $C$  is an arbitrary constant. The mean value of the kinetic energy of the electron during the vibration is

$$T = \frac{e^2}{2a} \left(1 \mp 2E \frac{a^2}{e}\right). \quad . \quad . \quad . \quad . \quad (16)$$

Leaving aside for a moment the discussion of the possibility of such orbits, let us investigate what series of stationary states may be expected from the expressions (14) and (15). In order to determine the stationary states we shall, as in the former section, seek a connexion with ordinary electrodynamics in the region of slow vibrations. Proceeding as on page 509, suppose when  $n$  is large

$$\frac{dA_n}{dn} = h\omega_n,$$

where  $A_n$  and  $\omega_n$  denote the energy and the frequency in the  $n$ th state. By help of (14) and (15) we get

$$\frac{dn}{da} = \frac{\pi e \sqrt{m}}{h \sqrt{a}} \left(1 \mp \frac{5}{2} E \frac{a^2}{e}\right).$$

This gives 
$$n = \frac{2\pi e \sqrt{m}}{h} \sqrt{a} \left( 1 \mp \frac{1}{2} E \frac{a^2}{e} \right),$$

or 
$$2a_n = \frac{n^2 h^2}{2\pi^2 e^2 m} \left( 1 \pm E \frac{h^4 n^4}{16\pi^4 e^5 m^2} \right). \quad . \quad . \quad . \quad (17)$$

Introducing this in (14), (15), and (16) we get

$$\omega_n = \frac{4\pi^2 e^4 m}{h^3 n^3} \left( 1 \mp E \frac{3h^4 n^4}{16\pi^4 e^5 m^2} \right), \quad . \quad . \quad . \quad (18)$$

and

$$A_n = C - \frac{2\pi^2 e^4 m}{n^2 h^2} \left( 1 \pm E \frac{3h^4 n^4}{16\pi^4 e^5 m^2} \right), \quad . \quad . \quad (19)$$

$$T_n = \frac{2\pi^2 e^4 m}{n^2 h^2} \left( 1 \mp E \frac{3h^4 n^4}{16\pi^4 e^5 m^2} \right). \quad . \quad . \quad . \quad (20)$$

It should be remembered that these deductions hold only for large values of  $n$ . For the mechanical interpretation of the calculations we need therefore only assume that the eccentricity is very nearly unity for the large orbits. On the other hand, it appears from (17), (18), and (19) that the principal terms in the expressions for  $2a_n$ ,  $\omega_n$ , and  $A_n$  are the same as those deduced in the former section directly from the Balmer formula. If we therefore suppose that these quantities in the presence of an electric field can be expressed by a series of terms involving ascending powers of  $E \frac{a^2}{e}$ , we

may regard the above deduction as a determination of the coefficient of the second term in this series, and may expect the validity of the expressions for every value of  $n$ . It may be considered, in support of this conclusion, that we obtain the same simple relation (11) between the frequency of revolution and the mean value of the kinetic energy as was found without the field, *cf.* p. 510.

In the presence of an electric field we shall therefore assume the existence of two series of stationary states of the hydrogen atom, in which the energy is given by (19). In order to obtain the continuity necessary for a connexion with ordinary electrodynamics, we have assumed that the system can pass only between the different states in each series. On this assumption we get for the frequency of the radiation emitted by a transition between two states corresponding to  $n_2$  and  $n_1$  respectively :

$$\nu = \frac{1}{h} (A_{n_2} - A_{n_1}) = \frac{2\pi^2 e^4 m}{h^3} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \left( 1 \mp E \frac{3h^4}{16\pi^4 e^5 m^2} n_1^2 n_2^2 \right). \quad . \quad . \quad . \quad (21)$$

This formula gives for every hydrogen line two components situated symmetrically with regard to the original line. Their difference in frequency is proportional to the electric force and equal to \*

$$\Delta\nu = \frac{3}{4\pi^2} \frac{h}{em} E (n_2^2 - n_1^2). \quad . \quad . \quad . \quad (22)$$

According to the deduction of (21) we may expect that for high values of  $n$  the radiation corresponds to vibrations parallel to the electric force. From analogy with the above considerations and in order to obtain agreement with Stark's result we shall assume that this polarization holds also for small values of  $n$ .

Introducing in (21) the experimental values for  $e$ ,  $m$ , and  $h$ , and putting  $E=43.3$  corresponding to an electric force of 13,000 volt per cm., we obtain for the distance between the components of  $H_\beta$  ( $n_1=2$ ;  $n_2=4$ ) and  $H_\gamma$  ( $n_1=2$ ;  $n_2=5$ ),  $4.77 \cdot 10^{-8}$  and  $6.65 \cdot 10^{-8}$  cm. respectively. We see that these values are of the same order of magnitude as the distance observed by Stark between the two components polarized parallel to the electric force, viz.  $3.6 \cdot 10^{-8}$  and  $5.2 \cdot 10^{-8}$  cm. The values calculated are somewhat higher than those observed; the difference, however, might possibly be due to the difficulties, mentioned in Stark's paper, of the determination of the magnitude of the electric force in his preliminary experimental arrangement.

For the ratio between the displacements of  $H_\beta$  and  $H_\gamma$  we get from (21) 0.7168, independent of the magnitude of the electric force. It will be seen that this value agrees closely with that observed, viz.  $3.6/5.2$  or 0.69. In this connexion it may be noticed that the value calculated for the ratio in question is independent of the value of the numerical factor in the expression (21), and consequently of the detailed assumptions used in deducing this expression. The value for the ratio can be derived directly from the assumption of the existence of a series of stationary states, in which the energy can be expressed in terms corresponding to ascending powers of  $E \frac{a^2}{e}$ .

A possible origin of the feeble components polarized perpendicular to the field, which were observed by Stark, may

\* *Note added during the proof*—In the *Phys. Zeitschr.* of Feb. 1, A. Garbasso and E. Gebrecke (*cf.* note, p. 511) have deduced expressions for  $\Delta\nu$  which differ from (22) only by a numerical factor of 2 and 4/3 respectively. The arguments of Garbasso are stated very briefly, but seem of a type similar to those of the present paper. The line of arguments of Gebrecke differs essentially from that used here.

be found when a closer examination is made of the effect of the electric field on the motion of the electron\*. This problem, however, will not be considered further at this stage.

The problem of the influence of an electric field on the spectra of other elements is naturally far more complicated than for hydrogen, and cannot be discussed in detail until the theory for such spectra is further developed. It seems, however, possible on the present theory to obtain a simple explanation of the characteristic difference, observed by Stark, in the effect of the field on the lines of the different series of the helium spectrum.

According to the last section, the different series of lines in the spectrum of an element correspond to different series of stationary states of the atom in which one of the electrons moves in an orbit outside the others. For any high value of  $n$  this orbit is approximately the same as that of the electron in a hydrogen atom. In the discussion we assumed that the effect of an electric field on the energy of the stationary states of the hydrogen atom, is connected with a considerable variation in the position and eccentricity of the orbit of the electron in the presence of the field. The possibility of such a variation is due to the fact that without the field every elliptical orbit is stationary. When, however, there are perturbing forces from the inner electrons the latter condition is not satisfied, and thus the effect of an external electric field on the stationary states may be expected to be much smaller than for the corresponding states of the hydrogen atom.

A measure of this effect of the inner electrons on the motion of the outer may be obtained by considering the function  $\phi_r(n)$ . The nearer this function approaches unity the smaller is the disturbance due to the inner electrons, and the more the motion of the outer approaches to that of the electron in the hydrogen atom. Now for the elements of low atomic weight, such as helium and lithium,  $\phi_r(n)$  has a value very nearly unity for the Diffuse series, while for the Sharp series or the Principal series, the value is not at all as close. On our theory we should, therefore, expect a much greater influence of an electric field on the first series than

\* Note added during the proof.—In *Verh. d. Deutsch. Phys. Ges.* 1914, p. 20, K. Schwarzschild has discussed the problem of the effect of the field on the motion of the electron in some detail. In contrast to the above considerations he attempts to apply the results on the explanation of the Stark effect without leaving ordinary electrodynamics.



on the other two series. This is in agreement with Stark's experiments\*.

On the present point of view a line of the Diffuse series of the helium spectrum corresponds to a transition between two stationary states, one of which is affected by the presence of an electric field, and the other not: while for the hydrogen lines both states were assumed to be affected by the field. This circumstance may afford an explanation of the fact observed by Stark, viz. that the components of the helium lines were not polarized relatively to the field like the hydrogen lines.

### § 3. *The Effect of a Magnetic Field.*

An effect of a magnetic field on the line-spectrum of an element was discovered by Zeeman in 1896. By spectroscopic observation in a direction perpendicular to the field the lines are resolved, in the simplest case, into symmetrical triplets of which the central components have the same position as the original line and are polarized with electric vector parallel to the field, while the outer components are polarized with electric vector perpendicular to the magnetic field.

As is well known, Lorentz succeeded in explaining this result on the basis of the classical electron theory. According to his calculation, which was found to agree with Zeeman's observation within the limit of experimental error, the difference in frequency between the outer and the inner components is the same for every spectral line, and equal to

$$\tau = \frac{1}{4\pi} \frac{e}{cm} H, \quad . . . . . (23)$$

where  $H$  is the magnetic force and  $c$  the velocity of light.

Later more complicated types of magnetic effect on spectral lines have been observed. In most cases, however, simple numerical relations are found to exist between the distance † of the components observed and that calculated by Lorentz. Further, the recent experiments by Paschen and Back ‡ on the magnetic effect on double lines, which will be mentioned in the next section, indicate that the complicated types of Zeeman effect are intimately connected with complication

\* Since the value of  $\phi_r(n)$  differs widely from unity for all series of lines in the spectra of the heavier elements, it is to be expected that the electric effect should be very small, or undetectable for such elements.

† See C. Runge, *Phys. Zeitschr.* viii. p. 232 (1907).

‡ *Ann. d. Phys.* xxxix. p. 897 (1912), xl. p. 960 (1913).

of structure in the undisplaced lines. Theoretical explanations of these results have been proposed by Voigt\* and Sommerfeld†.

Since in the presence of a magnetic field the spectrum of an element cannot be expressed by a formula of the type (2), it follows that the effect of the field cannot be explained by considerations analogous to those employed in section 2 in considering the effect of an electric field. If we retain the principal assumption of stationary states, we must assume that a *magnetic* field exerts an influence on the mechanism of transition between the stationary states, and thereby on the relation between the frequency of the radiation and the amount of energy emitted (*cf.* p. 513). In order to investigate this problem we shall seek a connexion with ordinary mechanics in the region of slow vibrations, from analogy with the procedure of the former sections.

Consider an electron rotating round a positive nucleus of infinite mass. In the stationary states of the system the motion of the electron without any field will be an ellipse with the nucleus in the focus. Similarly, suppose that in the presence of a magnetic field the motion of the electron in the stationary states can be calculated in the ordinary way; then, according to a general theorem of Larmor‡, the orbit of the electron in the field will be a superposition of an elliptical orbit and a uniform rotation round an axis through the nucleus parallel to the magnetic force. This implies a neglect of terms proportional to the square of the magnetic force. The frequency of rotation is equal to  $\tau$  in (23). According to ordinary electrodynamics the radiation emitted by the rotating system will correspond to a Zeeman triplet, the central component of which has the same frequency as the frequency of revolution in the elliptical orbit. In addition, Langevin§ has shown that the total energy of the system is not altered by the rotation, since a possible gain in the kinetic energy of the electrons may be considered as balanced

\* *Ann. d. Phys.* xl. p. 368, xli. p. 403, xlii. p. 210 (1913).

† *Ann. d. Phys.* xl. p. 748 (1913).

‡ 'Æther and Matter,' Cambridge, 1900, p. 341.

§ *Ann. de Chim. et de Phys.* v. p. 70 (1905). In this connexion it may be remarked that on the present theory the rotation will give rise to diamagnetism only, since the kinetic energy of the electrons in the stationary states cannot be transferred into heat motion such as is supposed by Langevin in his theory of magnetism. This conclusion seems consistent with experiments which show that the monatomic gases helium and argon are diamagnetic (see P. Tänzler, *Ann. d. Phys.* xxiv. p. 931 (1907)), although the structure of these atoms, proposed in my former paper, was of a type which on Langevin's theory should show paramagnetism.

by a corresponding loss of potential energy of the whole system relative to the field.

In order, therefore, to obtain the connexion with the ordinary mechanics and at the same time to be in agreement with experiment \*, we are led to assume that the effect of a magnetic field on the stationary states of the hydrogen atom consists simply in a superposed rotation of frequency  $\tau$  round the axis of the field, and that the radiation emitted by the transition between two stationary states is changed by the field so as to have the polarization and frequencies of a Zeeman triplet. It will be seen that this assumption is equivalent to supposing that the energy of the hydrogen atom in its stationary states is not altered by the presence of the field, but that the relation (1) in case of vibrations perpendicular to the field is replaced by the relation

$$A_1 - A_2 = h(\nu \mp \tau). \quad . \quad . \quad . \quad . \quad . \quad (24)$$

The essential difference between these assumptions and those employed in explaining the effect of an electric field will be noticed †.

From the analogy between the explanation of the hydrogen spectrum and that of spectral series of other elements given in the first section, we may naturally assume that similar assumptions will hold for the stationary states of other atoms. A possible explanation on this basis of the complex Zeeman effect of double lines will be indicated in the next section.

#### § 4. Double Spectral Lines.

According to the considerations used in sections 1 and 2, each series of lines in the spectrum of an element corresponds to a series of stationary states of the atom, in which one of the electrons moves outside the others. The configuration of the inner electrons is assumed to be very nearly the same in each series, while that of the outer electron changes from

\* See Fr. Croze, *Journ. de Phys.* iii. p. 882 (1913).

† Note added during the proof.—In *Phys. Zeitschr.* of Feb. 15, K. Herzfeld has discussed in detail the different possibilities of the effect of a magnetic field which might be expected on the theory of the hydrogen spectrum proposed by the writer. His conclusions are equivalent with those obtained above. In addition he considers the effect of terms proportional to the square of the magnetic force and shows that in a strong magnetic field these terms may be expected to have an appreciable influence on the magnetic resolution of the hydrogen lines corresponding to high numbers in the Palmer series. This is a consequence of the large orbits of the electron in the stationary states corresponding to high values of  $n$ .



state to state approximately in the same way as that of the electron in the stationary states of the hydrogen atom.

On this interpretation we may naturally assume that the appearance of double lines in the spectra of many elements\* is due to small perturbing forces originating in the configuration of the inner electrons and having a different effect on the motion of the outer electron according to different positions of its orbits. From the fact that the frequency of the components of double lines can be expressed by a formula of the type (2), we may conclude, on the considerations of section 2 and 3, that the perturbing forces in question are of electrostatic and not of electromagnetic origin. As we shall see, this view seems to offer a simple explanation of the laws observed for the variation of the distances between the components in a series of double lines.

At a distance from the centre of the atom, great in comparison with the distances of the inner electrons, the total force due to the nucleus and the inner electrons will be very nearly equal to that from a nucleus of a single positive charge. At a distance  $r$  the force may be expressed by

$$\frac{e}{r^2} + \frac{P}{r^3} + \frac{Q}{r^4} + \dots, \dots \dots (25)$$

where  $P, Q, \dots$  may vary with the direction of the line from the nucleus to the outer electron, as well as with the time. The second term in (25) corresponds to a configuration of the inner electrons and the nucleus equivalent to an electric doublet. In case of such a configuration it will appear that the condition of dissymmetry necessary for a different effect on different orbits of the outer electron is satisfied. For configurations more symmetrical, in which the centre of gravity of the inner electrons coincides with that of the

\* The lines of the ordinary hydrogen spectrum from a vacuum-tube also appear as close doublets with high dispersion. Considering, however, the want of sharpness of the lines and the discrepancies between the distance of components found by different observers, it seems probable that the lines are not true doublets, but are due to an effect of the electric field in the discharge. This is also indicated by the fact that the distance between the components observed increases with the number of the line, contrary to the behaviour of ordinary double lines. The distance between the components observed by Paschen and Back (*loc. cit.*) was  $0.20 \cdot 10^{-8}$  cm. and  $0.24 \cdot 10^{-8}$  cm. for  $H_\alpha$  and  $H_\beta$  respectively. According to Stark's experiments on  $H_\beta$  this corresponds to a resolution produced by an electric force of about 900 volt per cm. The ratio between an electric resolution of  $H_\alpha$  and  $H_\beta$  should, according to the calculations of section 2, be 0.76; the ratio between the components observed is 20/24 or 0.83.



nucleus,  $P$  will be zero and the perturbing forces will be given by the higher terms in (25).

Let us now assume that for a certain series of stationary states  $P$  is different from zero. According to our considerations, the major-axis of the orbit of the outer electron is approximately equal to that in the stationary states of the hydrogen atom. The major-axis will therefore be approximately proportional to  $n^2$ . Accordingly the quantity corresponding to  $E$  in the equation (19) and due to the second term in (25) will vary approximately as  $n^{-6}$ . The difference in the energy of the two stationary states corresponding to (19) may therefore be expected to vary approximately as  $n^{-4}$ . This corresponds to the variation observed for the distances between the components of the double lines in the spectra of the alkali metals.

The visible spectra of the alkali metals consist of three series of double lines. The difference in frequency of the components of the lines of the Sharp series and the Diffuse series is the same for every line. For the Principal series the difference diminishes rapidly with the number of the line in the series, the difference being approximately proportional to the inverse fourth power of this number. It will appear that this spectrum can be interpreted on the assumption of three series of stationary states of the atom, corresponding to different configurations of the inner electrons; viz.: two single series I. and II., and a double series III. representing for every  $n$  two stationary states for which the difference in energy varies in proportion to  $n^{-4}$ . The Principal series of doublets corresponds to a transition from a pair of the states III. to the first state of I., while the Sharp and Diffuse series correspond to transitions respectively from states I. and II. to the first pair of state III.

I shall not here try to develop these considerations in further detail, but confine myself to show that the view adopted seems to indicate a possible explanation of the results of the experiments by Paschen and Back on the effect of a magnetic field on spectral lines of complicated structure. The characteristic result of these experiments is the great difference between the effect of a weak and a strong magnetic field. In the presence of a weak magnetic field the components of a double line are resolved in a complicated way. If the field increases, the distances between the sub-components at first increase regularly with the strength of the field. When, however, the distances are of the same order of magnitude as the distance between the components of the original double line, the aspect of the system of lines

gradually alters. The single lines get diffuse and grow together; and when the field is increased still more the whole system of lines tends to shrink into three homogeneous components, with the same relative positions as the components of a simple Zeeman triplet.

An analogy to these results is obtained by considering the simultaneous effect of an electric and a magnetic field on a system consisting of an electron rotating round a nucleus of infinite mass. In section 2 we assumed that the effect of an external electric field is to increase the eccentricity of the orbit of the electron and to direct the major-axis parallel to the electric force. According to section 3, the effect of a magnetic field is to superpose a rotation of uniform frequency on the orbit of the electron. To consider the simultaneous effect of electric and magnetic fields the axes of which are perpendicular to each other, let us first suppose that the effect of the electric force is large compared with the effect of the magnetic force. In this case, the directing effect of the electric force will oppose the rotatory effect of the magnetic force, and the result may be the appearance of a number of stationary orbits close to the orbits to be expected when the electric field acts alone. If, on the other hand, the effect of the magnetic field is large compared with that of the electric field, the directing effect of the latter cannot prevent the general rotation of the system, and it is easily seen that the case will be very similar to that due to the magnetic field alone. The necessary condition for the application of this analogy to the case of the magnetic effect on double lines, is that the configuration of the inner electrons does not rotate in the field with the same frequency as the orbits of the outer electrons. It may be noticed that these considerations bear an analogy to the theory of Sommerfeld (*cf.* p. 519), which corresponds to the analogy between the considerations of the former section and the theory of Lorentz.

#### *Concluding Remarks.*

In the deductions of this paper the following general assumptions are used :—

1. That an elementary system containing rotating electrons will not emit energy radiation in the continuous way assumed in ordinary electrodynamics, but that radiation is only emitted during the passing of the system between a certain number of stationary states.

2. That the dynamical equilibrium of the system in the

stationary states is governed by the ordinary laws of mechanics, while these laws do not hold for the passing of the system between the different stationary states.

3. That the radiation emitted during the passing of the system between two stationary states is homogeneous; and that only in the region of slow vibrations does the frequency approach that to be expected on ordinary electrodynamics, while in general the frequency  $\nu$  is determined by the relation  $E = h \cdot \nu$ , where  $E$  is the total amount of energy emitted and  $h$  Planck's constant.

It has been attempted to show that, applying these assumptions to Rutherford's theory of the structure of atoms, it seems possible to obtain an explanation of the laws of line-spectra discovered by Balmer, Rydberg, and Ritz.

It has further been attempted to show that it seems possible to account for some of the general features of the effect of magnetic and electric fields on spectral lines discovered by Zeeman and Stark. In the case of an electric field it is assumed that no alterations in the above assumptions take place. In the case of a magnetic field, however, it is found necessary to modify the third assumption in order to retain the connexion with ordinary electrodynamics in the region of slow vibrations.

LX. *Separation of Close Spectrum Lines for Monochromatic Illumination.* By R. W. WOOD, *Professor of Experimental Physics, Johns Hopkins University, and Adams Research Fellow of Columbia University*.\*.

[Plate VII.]

IN many branches of research in physical optics it often becomes necessary, for one reason or another, to separate two or more close spectrum lines, utilizing the light of one only.

For example, in experiments upon the monochromatic excitation of resonance spectra, the line utilized for the illumination of the fluorescing vapour must be isolated either by absorbing screens or by a spectroscope, used as a monochromator.

If the latter method is employed the illumination is much restricted by the necessity of employing a slit, or rather two slits; and in the case of close spectrum lines, such as the D lines of sodium, the necessity of employing very fine slits makes it very nearly impossible to accomplish anything in

\* Communicated by the Author.



this way. Even in the case of the three green copper lines, I found the greatest difficulty in getting sufficient illumination with a single line isolated by means of a very large monochromator of 1.5 metres focus.

In the present paper I shall give a method which enables us to utilize a source of light of large size, say  $1 \times 3$  cm., and remove one or more lines from it with *practically no loss of light*.

For example, we can form two images of a sodium flame by means of a condenser having an effective aperture equal to  $f^2$ , one image containing only the light of wave-length 5890, the other only light of wave-length 5896, both images being very nearly as intense (with respect to *one* sodium line) as if the condenser had been employed without the separating apparatus.

The method is an improvement upon one which I used many years ago in the study of the dispersion of sodium vapour and described briefly at that time. It is a polarization method, and may be described briefly as follows.

If plane-polarized monochromatic light is passed through a plate of some doubly refracting crystal with its direction of vibration making an angle of  $45^\circ$  with the axis, it will emerge plane-polarized parallel to the original plane for certain thicknesses of the plate, and plane-polarized at a right angle to this plane for other thicknesses. For intermediate thicknesses it will be elliptically or circularly polarized.

If we employ a plate of quartz 30 mm. thick the emergent waves of  $D_1$  and  $D_2$  of sodium will be plane-polarized at right angles to each other, and either can be quenched by a nicol suitably oriented. If white light is used, and analysed by a spectroscope, the spectrum will be furrowed by dark bands, the distance between a bright and a dark band being, in the yellow region, 6 Ångström units, the distance between the D lines.

As it was desired to utilize this principle for the separation of the D lines for the purpose of exciting the resonance radiation of sodium vapour by the light of  $D_1$  and  $D_2$  separately, by which means we may determine whether the mechanisms which give rise to the radiations are coupled together, an investigation which is being carried to a successful conclusion in collaboration with L. Dunoyer at the present time, it became necessary to bring the method up to the highest possible efficiency. As it is necessary to employ a large condenser and work with very divergent and convergent cones of light, a block of quartz of very large size



must be used, placed between the two halves of the condenser, since the rays which traverse the block must be parallel. If this is not the case, different pencils will traverse different thicknesses, and will be differently polarized. Moreover, one half of the light is lost at the start by the polarizing nicol. This difficulty was overcome by employing a large double-image prism, and subsequently analysing by a double-image prism. In this way, with proper orientation of the prisms, the two images containing only  $D_2$  light were superposed, the  $D_1$  images (of one half the intensity) lying to the right and left. By this expedient the  $D_2$  image had the full intensity, except for the loss by reflexion from the six transparent surfaces of the prisms and quartz block.

A rotation of  $90^\circ$  of the plane of polarization is produced by a quartz plate  $\cdot 032$  mm. in thickness for sodium light, consequently the plate must be plane-parallel to within considerably less than this distance, otherwise  $D_1$  will be passed by some parts of the field and  $D_2$  by others. If the difference in thickness changes by  $\cdot 032$  mm. in passing from one edge of the block to the other, one edge will transmit  $D_2$  only, and will appear brighter than the other edge which transmits only  $D_1$ , while the centre of the plate will transmit both  $D_1$  and  $D_2$  in a state of circular polarization. Here both wave-lengths will be passed by the analysing nicol, and the intensity will be intermediate between the values at the edges. If the thickness varies at a more rapid rate, bright and less bright bands will cross the field, the bright bands containing  $D_2$ , the less bright  $D_1$ .

The calculated value  $\cdot 032$  mm. was verified with a fragment of a quartz plate 30 mm. in thickness and slightly wedge-shaped, placed at my disposal by Mr. Twyman, manager of the firm of Adam Hilger & Co., who also loaned me the quartz echelon used in the preliminary investigation. With this block between crossed nicols seven bands were counted (counting both dark and bright). This means that we pass from  $D_1$  to  $D_2$  transmission seven times in crossing the plate. Multiplying the calculated thickness  $\cdot 032$  mm. by seven gives us  $0\cdot 224$ , while the difference in thickness of the plate at the two edges, as measured with the spherometer, was found to be  $0\cdot 243$ .

An investigation was also made with an echelon of quartz placed with its elements horizontal between the nicols. It was illuminated with a sodium flame, and an image of the steps thrown upon the slit of a spectroscope. Each element of the slit covered by an echelon step is thus illuminated by light which has traversed a different thickness of quartz.

At some points only  $D_1$  appeared, at others only  $D_2$ , while at others both  $D_1$  and  $D_2$  were found.

The polarizing nicol is of course placed with one of its *diagonals* making an angle of  $45^\circ$  with the vertical. A photograph of this phenomenon is reproduced on Pl. VII. fig. 1. The best separation of  $D_1$  and  $D_2$  was given by step no. 6, and as each plate was 4.7 mm. in thickness, the total thickness was  $4.7 \times 6$  or 28.2 mm. The seventh step showed both  $D_1$  and  $D_2$ , as the total thickness here happened to be that giving circular polarization for both wave-lengths. A slight inclination of a plate of this thickness would cause it to transmit  $D_1$  or  $D_2$  only, by changing the length of the optical path in quartz.

In practice we may use a plate anywhere between 25 and 40 mm. in thickness. The best thickness is 32 mm., which gives us the maximum intensity for either sodium line when the other is cut off. With a plate of say 25 mm. in thickness  $D_1$  can be completely extinguished, but the transmitted light ( $D_2$ ) will not be as bright as when a plate of the correct thickness is used.

If the echelon is illuminated with white light, the continuous spectrum transmitted by each step is furrowed by black bands, which represent wave-lengths of light vibrating parallel to the long diagonal of the analysing nicol. The distance between the bands decreases with the number of plates which operate at each step. A photograph of these bands with the D lines superposed is reproduced on Pl. VII. fig. 4.

For a thickness equal to 32 mm. the distance between adjacent bright and black bands is 6 Ångström units. If a different thickness is employed, and a black band brought into coincidence with  $D_1$ ,  $D_2$  will lie a little to one side of the centre of the adjacent bright band and its intensity will be less than if the correct thickness is employed.

The extinguishing of one of the D lines can be shown with a natural uncut crystal of quartz, if the surfaces are fairly good. The crystal is to be placed between crossed nicols, utilizing two opposed surfaces, which are separated by a distance of two or three centimetres.

An image of the crystal is projected upon the slit of the spectroscope, and  $D_1$  will be found absent at certain points,  $D_2$  absent at others. It is another matter if a large amount of light is to be used, as in experiments upon fluorescence, for in this case we must use a large block of uniform thickness *free from all traces of crystalline irregularities.* Brazilian

quartz should be used, as the crystals from Madagascar show irregularities when examined by polarized light.

A large and very clear crystal was selected and examined between crossed nicols with sodium light. There appeared to be no internal irregularities of a nature such as were exhibited by a beautiful block of quartz loaned to me by Mr. Twyman, which was possibly cut from a Madagascar crystal. In this block the  $D_1$  and  $D_2$  bands, instead of appearing uniformly parallel, were deformed at one point in sharp zig-zags; no trace of anything could be seen by unpolarized light. It is not always possible to judge a crystal before it is cut, but if the faces are reasonably plane and clear, it is usually possible to tell whether variations in the intensity of the sodium light result from internal troubles, or from small differences in thickness. From the selected crystal a block measuring 85 mm.  $\times$  60 mm.  $\times$  32 mm. was cut parallel to the axis and polished\*.

As the degree to which the plate needs to be plane-parallel can easily be attained by the use of the spherometer, and as the side faces do not have to be accurately parallel to the axis, the preparation of the plate presents no great difficulty.

It was examined with sodium light between crossed nicols before the polishing stage was reached, and found to give absolutely uniform illumination, which is what is required. Glass plates and benzine were of course used to render the block transparent. M. Bertin increased the uniformity of thickness considerably even after this test, and then polished the six surfaces of the block. This block when used for separating the D lines (32 mm. thickness) has an area of 50 square cms. Used in the other position, 60 mm. thickness, it will separate lines 3 Ångström units apart. Used "end-on" its property of natural rotation can be utilized in certain experiments.

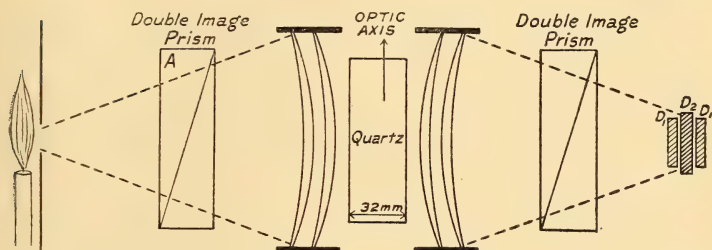
The double refraction of Iceland spar is very much greater than that of quartz, a plate less than 3 mm. thick being required for the D lines. It would, however, have to be plane-parallel to a degree 10 times as great as is the case with quartz. A thick block of spar, made plane-parallel by the methods in use in the construction of modern interferometers, could very likely be used for suppressing the strong central components of multiple lines, when photographing or examining the fainter satellites. Experiments in this direction are now in progress.

\* The work was done by M. Bertin, 13 quai St. Michel, Paris, whom I have instructed as to the methods of testing by polarized sodium light. The price of the crystal, including cutting and polishing, was 140 francs.



The quartz plate has proved most satisfactory in every respect. Placed between the two halves of a Dunoyer condenser of 10 cm. diameter and 12 cm. focus for parallel light (*i. e.* 24 cm. focal length when forming an image of a source of light equal in size to that of the source), it is possible to utilize the entire 50 square cm. of the plate in forming an image of the aperture ( $1 \times 3$  cm.) placed before the sodium flame, containing only  $D_1$  or  $D_2$  light.

The arrangement of the apparatus is shown in the diagram.



The double-image prism A is so oriented as to have the vibrations of the two transmitted beams at  $45^\circ$  with the vertical. The second double-image prism is oriented *in the absence of the quartz block*, so as to give two images of the source side by side, and separated by a distance equal to the width of each image. Each image contains both  $D_1$  and  $D_2$ . If now the quartz block is placed between the two halves of the condenser, all of the  $D_2$  light (for example) leaves the original images, and unites into a third image between the other two. This is the image utilized. If it is desired to have  $D_1$  light in this image, it is necessary only to rotate the block a degree or to, thereby increasing the optical path in quartz. If we rotate the analysing double-image prism the central image splits up into two, and the correct position of the prism can be determined by bringing these two images into exact coincidence. As I have said previously, this method obviates the 50 per cent. loss of light which results from the use of Nicol's prisms. As the double-image prisms had apertures considerably less than that of the quartz block, they were placed midway between the condenser lenses and the image and source, as shown in the figure. With prisms of too small aperture, however, placed close to the source and image, the separation of the images would be insufficient.

To test the adjustment of the quartz block and the general efficiency of the apparatus, we have only to receive the three images upon a piece of white paper, and project an image of



the central one upon the slit of a spectroscope capable of clearly resolving the D lines.

If the optic axis is not vertical some parts of the slit will be illuminated with  $D_1$ , others with  $D_2$ , and others with both  $D_1$  and  $D_2$ , as shown by the photograph reproduced on Pl. VII. fig. 2.

The completeness of the extinction is seen from the very faint trace of  $D_1$  seen at the regions where  $D_2$  only was transmitted. A very fine slit was used, and the plate over-exposed.

The block must be tilted forwards or back until the same condition obtains all along the slit. The block is now rotated slightly until either  $D_1$  or  $D_2$  is completely quenched. We can now be sure that the image is made up entirely of monochromatic light, as shown in fig. 3, in which the upper portion of the slit is illuminated by  $D_2$  light, and the lower by the light of the sodium flame.

For work with the spectroscope alone, in which cones of light of large aperture are not needed, a quartz echelon answers every purpose, so that this instrument, recently placed on the market by the Hilger Co., may be utilized in a new way.

The experiments outlined in the present paper were carried on at the Sorbonne, in the laboratory of Monsieur Bouty, who placed every facility at my disposal.

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LXI. *Note on the Production of a very intense Sodium Flame.* By R. W. WOOD\*.

IN the course of the experiments described in the preceding paper, it was found desirable to have an exceedingly intense sodium flame available for the adjustment of the quartz block for the complete extinction of one of the D lines.

As a flame of this description is often desirable in many branches of optical work, it has seemed worth while to add a separate note on the subject.

The intensity of a soda flame depends chiefly upon the rate at which the sodium molecules are delivered into the flame, that is the rate at which the chloride of sodium is volatilized. If a small fragment of the mantle of a Welsbach light is laid upon the grill of a Meker burner, and two or three small fragments of fused sodium chloride are placed on

\* Communicated by the Author.

this, on lighting the burner a flame of a most astonishing brilliancy is at once formed. So rapid is the evaporation of the chloride that clouds of smoke rise from the flame, and the intensity, while at its maximum, appears to be as great as that of the oxy-hydrogen sodium flame, which is much more difficult to manage. The simplicity of this method makes it immediately available in any laboratory. The function of the scrap of mantle is of course to spread the material over a large surface of very small heat capacity, so that it can be brought to the temperature of the hottest part of the flame. The bead melts and the mantle acts like the wick of a lamp.

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LXII. *A Photometric Study of the Fluorescence of Iodine Vapour.* By R. W. WOOD and W. P. SPEAS\*.

THE reduction in the intensity of the fluorescence of iodine vapour caused by the admixture of air or other foreign gas was studied by one of the present writers a number of years ago (Wood, *Phil. Mag.* xxi. p. 309, 1911); and subsequently Wood and Franck (*Phil. Mag.* xxi. p. 314, 1911) discovered that the gases which were strongly electro-negative were the most effective in reducing the intensity of the fluorescence. Of all the gases studied the least effective was helium, the intensity of the fluorescence of the iodine vapour, when mixed with helium, even at two or three centimetres' pressure, being almost as great as *in vacuo*. The colour of the fluorescent light was changed, however, from yellowish-green to orange-red by the presence of the helium; and the curves obtained showed that this resulted from the circumstance that the helium reduced the intensity of the radiations of shorter wave-length in the fluorescent spectrum to a greater degree than the less refrangible radiations. The extensive investigations of the remarkable resonance spectra emitted by the vapour when excited by monochromatic light, which have been carried on during the past two years by one of us, made a further photometric study desirable; for it appeared probable that careful determinations of the variation of the intensity of the radiations with the density of the iodine vapour would throw some light upon certain obscure points: for example, the circumstance that the faint band-spectrum which accompanies the resonance spectrum is more strongly developed when the iodine vapour is at very

\* Communicated by the Authors.

low density, the tube being cooled by ice. Moreover, it is of considerable interest to determine to what extent the luminosity of an iodine molecule is diminished by the proximity of other iodine molecules; in other words, to determine the effect of *iodine* vapour at different pressures upon the intensity of the iodine fluorescence, for comparison with the effects of the various other gases determined in the earlier work.

In the present case, however, the matter is complicated by the circumstance that an increase of pressure increases the number of fluorescing molecules.

It has been found possible, however, to allow for this circumstance and construct a curve showing the destructive action of iodine vapour upon the fluorescence of iodine vapour, precisely analogous to the curves constructed for helium, argon, nitrogen, hydrogen, &c. in the earlier investigation.

The iodine vapour was contained in an exhausted glass tube of the same form as those used in the study of the resonance spectra. The image of a quartz mercury arc formed along the axis of the tube by a large condenser excited a fluorescence of very constant intensity, which was measured by a photometer viewing the fluorescent vapour column "end-on."

The photometer was of the same type as that used in the earlier work, the comparison source being a white screen illuminated by the light of a Welsbach mantle passed through suitable filters for the purpose of matching the yellowish-green colour of the fluorescence. The temperature of the tube was raised by a water-bath, or lowered by the immersion of a small lateral tube in a bath of alcohol contained in a small Dewar cup and cooled to any desired temperature by the addition of liquid air. The density of the iodine vapour is determined by the temperature of the coldest part of the system, so that when working below room-temperature it was necessary to vary only the temperature of the small lateral tube.

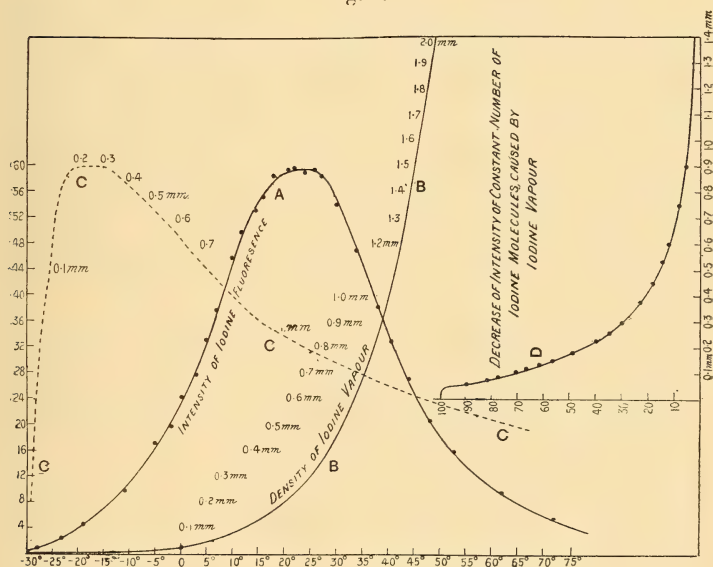
It was found that a measurable fluorescence was obtained even with a density corresponding to  $-30^{\circ}$  C. It was impossible, however, to obtain an absolutely black background, even with the end of the tube painted black for a distance of 10 cm. To determine the small amount of diffused and reflected light sent out by the background, it was only necessary to immerse the lateral tube in liquid air, which removed every trace of iodine vapour from the observation

tube, and measure the intensity of the very feeble illumination of the background. This constant quantity was subtracted in each case from the measured intensity of the fluorescence.

When working above room-temperature, the entire tube was immersed in a rectangular glass tank filled with distilled water at the desired temperature.

The variation of the intensity of the fluorescence as a function of temperature is shown by curve A, fig. 1,

Fig. 1.



ordinates representing intensities and abscissæ temperatures. It is to be understood, of course, that the alteration of the temperature influences the intensity of the fluorescence only by changing the vapour-density.

The variation of the density of the iodine vapour with the temperature is shown by curve B, the pressures in millimetres of mercury (ordinates) being indicated to the left of the curve. This curve was plotted from the values obtained by Baxter, Hickey, and Holmes (*J. American Chemical Soc.* xxix. p. 127, Feb. 1907) between  $0^{\circ}$  C. and  $55^{\circ}$  C. They give no values below  $0^{\circ}$ , though a faint fluorescence can be observed at  $-30^{\circ}$ , to which point I have carried the curve by rough extrapolation.



The intensity curve A is remarkably symmetrical, with its maximum at  $20^{\circ}$ – $25^{\circ}$ . As we increase the temperature from  $-30^{\circ}$  to  $0^{\circ}$  the intensity increases, probably very nearly in proportion to the increase in pressure, since at these very small densities the intensity of the radiation given out by a molecule is not diminished by the presence of its neighbours. Above  $0^{\circ}$ , however, the increase is no longer proportional to the increase in the number of molecules, since the vapour begins to destroy its own fluorescence in the same way as would another gas, such as nitrogen or carbonic acid, only to a very much greater degree. For example, at a pressure of 0.05 mm. (at  $5^{\circ}$  C.) the intensity is 33, while at a pressure of 0.1 mm. (at  $11^{\circ}$  C.) the intensity is but 46, instead of 66, which is the value which we should expect if there were no interaction between the molecules. Between  $17^{\circ}$  and  $25^{\circ}$ , though the number of molecules more than doubles, there is no increase in the intensity, the increase in the number of radiating molecules being almost exactly compensated by diminution in the intensity of the radiation from each one which results from the presence of its neighbours. Above  $25^{\circ}$  the reduction of intensity preponderates, and the curve falls rapidly.

If we plot the intensities (ordinates) against pressures (abscissæ) we obtain curve C (dotted), the pressures (abscissæ) being recorded along the curve. This curve gives us a better idea of the phenomenon than curve A, since in this case the intensities are plotted directly against the changes in the physical state which influences the radiation. This curve shows us, however, only the change in the intensity of the *total radiation* emitted by all the molecules with increase of pressure.

In view of the previous work, in which the diminution in the intensity of the radiation from a constant number of iodine molecules resulting from the presence of foreign molecules was investigated, it is of great interest to *determine to what extent the radiation from a given group of iodine molecules is diminished by interpolating other molecules of the same kind*, or, in other words, the effect of iodine vapour in reducing its own fluorescence as compared with the effect of other gases.

This can be done very easily by combining the values shown by curves A and B in the following way.

At a temperature of  $0^{\circ}$  the pressure is 0.03 mm. and the intensity of the fluorescence is 24. We wish now to determine the intensity of the radiation of this *same group of*

molecules, when an equal number of similar molecules has been interpolated. We raise the temperature to  $7^{\circ}$ , the pressure doubles ( $\cdot 06$  mm.), and the intensity increases to 36. We have, however, measured the radiation from all of the molecules, and we are concerned only with that which is emitted by the original group, which contributes one half of the measured intensity; consequently we must divide the 36 by 2, which gives us 18. The intensity of the radiation of the group has been reduced from 24 to 18 by an *increment* of pressure equal to  $\cdot 03$  mm.

At a temperature of  $11^{\circ}$  the pressure is  $\cdot 09$  mm. and the intensity is 47, one third of which, or 15.7, is contributed by the original group; consequently the intensity is reduced from 24 to 15.7 by a pressure increment of  $\cdot 06$  mm.

We can in this way construct a curve showing the decrease in intensity resulting from the interaction between the molecules.

It is to be noted, however, that we must choose, for the original group, a mass of vapour at a pressure below that at which the action of one molecule upon the radiation from a neighbouring one is appreciable.

If we take as our starting-point the intensity 12, at a pressure of  $\cdot 015$  mm. we find that at  $\cdot 03$  mm. the intensity is 24: one half of this is 12, our original value—in other words, *no reduction in intensity has resulted* from an increment of pressure of  $\cdot 015$  mm. At  $\cdot 045$  mm. the intensity is 30, one third of which is 10, a slight reduction having occurred.

In this way curve D was computed, the values calculated being multiplied by  $8\frac{1}{3}$  so as to make the intensity of the radiation from the vapour at the lowest pressure equal to 100. This curve shows us the extraordinary effect of iodine vapour upon its own fluorescence, the vapour at 1 mm. pressure reducing the intensity from 100 to 5.

It is interesting to compare the action of iodine vapour with that of the gases and vapours studied in the earlier work. In these other cases a constant temperature was employed, with the result that the iodine vapour density remained unchanged, and the intensity of the fluorescence was measured when various gases at different pressures were introduced into the bulb.

The intensity is reduced from 100 to 19 by hydrogen at 24 mm., by air at 11 mm., by  $\text{CO}_2$  at 7 mm., by ether vapour at 3 mm., by chloride of iodine at 1.8 mm., and *by iodine vapour* at a pressure of only 0.4 mm.

It is probable that chlorine would be still more effective than iodine, as it is more strongly electro-negative. The value given above for chloride of iodine is the value given in the earlier paper for chlorine, the fact having been overlooked that the vapours unite to form the compound when mixed. There was always an excess of iodine in the bulb, so that there is little doubt but that the correct interpretation of the experiment is to consider the active vapour iodine chloride instead of iodine.

Bromine vapour is more electro-negative than iodine, and though it has an absorption spectrum similar to that of iodine, its action in destroying its own fluorescence is so powerful that it is only possible to observe fluorescence at pressures probably in the vicinity of  $\cdot 001$  mm., the intensity then being so small that it is only with difficulty that the phenomenon can be detected. Sunlight must be focussed at the centre of the exhausted bulb, and the bromine vapour condensed by applying solid  $\text{CO}_2$  to the exterior : just before the last trace of vapour is condensed, there is a very feeble green fluorescence, of about the intensity of that shown by iodine vapour at  $-30^\circ$ .

The results obtained with iodine vapour at varying pressure emphasizes the following general statement made in the earlier paper :—

“In order to obtain a visible fluorescence we must have a sufficient number of molecules present : their number must not, however, be so great as to cause them to disturb each other. The pressure at which maximum fluorescence occurs depends upon the electrical character of the molecule.”

#### *Absorption of the Fluorescent Light by Iodine Vapour.*

It is obvious that, for a correct interpretation of the results found with the photometer, determinations of the absorbing power of the vapour for the fluorescent light must be made, since in all of the experiments the fluorescent light is obliged to traverse a greater or less amount of absorbing vapour.

The colour of the fluorescent light is distinctly red with dense vapour, orange-yellow at room-temperature, and yellow with a suggestion of green at the lowest temperatures. While this change is due in part to absorption of the green portion of the spectrum of the emitted light, there is undoubtedly another factor at work. In the earlier investigation it was found that the colour was changed very markedly



to red by the admixture of helium with a constant amount of iodine vapour, the same effect being observed in decreasing degrees with argon, hydrogen, and nitrogen. No change of colour was, however, observed when the intensity was reduced by chlorine. The suggestion was made that a foreign gas reduced the intensity of the fluorescence in two ways—by its electro-negative quality (the reduction in this case being unaccompanied by change of colour), and by collisions, which reduced the intensity of the short waves more than that of the long. It is quite possible that the collisions weaken what have been termed the resonance radiation lines more than the lines of increased wave-length.

In the case of the weakening of intensity by iodine vapour, the change of colour is probably largely due to absorption, since measurements showed that the fluorescent light was more strongly absorbed by iodine vapour than light of the same colour obtained by filtering the light of the Welsbach light through suitable colour-filters. This results from the circumstance that the fluorescent spectrum is discontinuous, some of its lines coinciding with absorption-lines. If the two fields of the photometer were matched, one being illuminated with the fluorescent light, the other with the filtered white light, the balance was destroyed if a bulb containing iodine vapour was held between the eye and the photometer. Measurements were also made by restricting the length of the illuminated column of iodine vapour by means of screens, illuminating first the end of the tube farthest from the photometer, and then the nearer end.

The actual intensity of the fluorescence was the same in the two cases, but in the former, owing to the greater thickness of the layer of iodine vapour traversed by the emitted light, the measured intensity was less.

The results indicated that the portions of the illuminated column nearest the photometer contributed more to the intensity than the portions farther away.

It was found that the absorption was much stronger for the fluorescence of the vapour at  $0^{\circ}$  than at room-temperature, amounting to 43 per cent. in the former case and 29 per cent. in the latter, for a layer of iodine vapour at  $23^{\circ}$  14 cm. in thickness. The absorption was brought about by inserting an exhausted bulb, 14 cm. in diameter, containing iodine crystals, between the fluorescent tube and the photometer. Instead of removing the bulb, to determine the intensity without absorption, the iodine vapour was condensed by the application of cotton wet with liquid air. In this way



the loss due to reflexion by the walls of the bulb was eliminated.

The effect of absorption will be to cause a decrease in the intensity of the fluorescence with increasing vapour-density. The effect is somewhat complicated by the circumstance that the green portion of the spectrum is more strongly absorbed than the red. This will cause a change in the colour of the fluorescence, apart from the cause already mentioned, namely collisions with other molecules. The intensity curve consequently falls more rapidly than it would if absorption were absent. It is not very easy to correct for absorption, since the light from each element of the column of vapour illuminated is obliged to traverse a different thickness of vapour.

The chief cause of the diminution of intensity is the mutual action between the molecules. There is no trace whatever of superficial fluorescence, or a glowing of a thin layer of the vapour in contact with the wall. This would be practically uninfluenced by absorption. It is present in a very marked degree with mercury vapour, both for the visible fluorescence, obtained by illuminating the dense vapour contained in a heated quartz bulb with the light of the spark, and the ultra-violet resonance radiation, stimulated at pressures below 1 mm. by the 2536 line of the mercury arc, as has been shown recently by one of the writers.

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### LXIII. *Proceedings of Learned Societies.*

#### GEOLOGICAL SOCIETY.

[Continued from p. 224.]

January 7th, 1914.—Dr. Aubrey Strahan, F.R.S., President,  
in the Chair.

THE following communications were read :—

1. 'The Ordovician and Silurian Rocks of the Lough Nafooev Area (County Galway).' By Charles Irving Gardiner, M.A., F.G.S., and Sidney Hugh Reynolds, M.A., F.G.S., Professor of Geology in the University of Bristol.

The Lough Nafooev area is a direct continuation of the Kilbride area (described in 1912), from which it is separated by the Finny River. It forms a ridge about 4 miles long, which reaches its highest point (1678 feet) at Curraghrevagh Mountain, and slopes steeply down to Lough Nafooev on the north, and more gradually to Glen Trague on the south.

The rocks are of Arenig, Llandeilo, and Silurian age, together with intrusive felsites, bostonites, labradorite-porphyrates, and dolerites.

The Llandeilo rocks (Mweelrea Grits and Conglomerates) are mainly confined to the low-lying ground along the shore of Lough Nafooev, and have yielded no fossils. They dip at a high angle off the Arenig rocks, which extend in a band from a third to half a mile wide from end to end of the area. The Arenig rocks consist in the main, as at Kilbride, of spilite-lavas associated with coarse breccias, and with bands and patches of chert in which at two points radiolaria were found. The Lough Nafooev area agrees with those of Glensaul and Tourmakeady in the presence of limestone-breccias which were absent at Kilbride. Unfortunately, no graptolites were found in the Arenig rocks of Lough Nafooev. Pillow-lavas show a splendid development, especially near the top of Bencorragh. Silurian rocks form the whole southern half of the area, including the highest point, Benbeg (1788 feet). They are very highly inclined, being (for much of their extent) vertical or sometimes slightly overfolded. They include representatives of the Llandovery, Tarannon, and Wenlock formations, and exhibit the same general succession as at Kilbride, although the relative thicknesses of the several bands are not the same. The occurrence of *Monograptus galaensis* on the north-eastern slopes of Benbeg confirms the field-evidence as to the Tarannon age of certain grey flags. The Wenlock beds, as at Kilbride, are represented by thick grits (Doon Rock Grits), a thickness of over 800 feet being seen. Of the intrusive rocks, felsites are not so prominent as at Kilbride, and, while at that locality they are always associated with Arenig rocks, at Lough Nafooev some are clearly of later date—occurring in the Llandeilo formation, or along the line of junction of the Llandeilo and other rocks.

The bostonite-sill seen at the base of the Silurian rocks at Kilbride extends almost continuously throughout the Lough Nafooev area, but is much reduced in thickness. Other small intrusions of bostonite occur in addition to this sill, which, as at Kilbride, is associated in places with labradorite-porphyrates. The prevalence of mica-dolerite intrusions in the purple shale (Tarannon) is a noteworthy feature.

The paper concludes with a table comparing the rocks of the Lough Nafooev area, on the one hand with those of Kilbride, and on the other with those of the Killary district described by Mr. R. G. Carruthers and Mr. H. B. Maufe.

2. 'The Geology of the St. Tudwal's Peninsula (Carnarvonshire).' By Tressilian Charles Nicholas, B.A., F.G.S.

The St. Tudwal's Peninsula is situated at the south-eastern extremity of South-West Carnarvonshire (Llyn), and forms the north-western limit of Cardigan Bay; it is underlain by Cambrian

and Ordovician rocks. In the southern part of the peninsula the structure is relatively simple, and the succession very plainly displayed in numerous cliff-sections; Cambrian rocks very similar in character to those of Merionethshire form most of the coast, but the interior is mainly occupied by Arenig beds, which rest with a marked unconformity on every local member of the Cambrian in turn. The latter have fortunately escaped cleavage, and some mudstones in the midst of the series have yielded a number of fossils belonging to the zone of *Paradoxides hicksi*. The *P.-davidis* Zone appears to be absent, as the result of a slight unconformity.

This southern area, of relatively simple structure, is separated by an overthrust of considerable magnitude from a more northern area in which members of the Tremadoc, Arenig, and Llandeilo Series have been recognized, but in which the rocks are highly crushed, faulted, and disturbed, and the relations between the beds are far from clear.

The general succession is :—

South of the Thrust.	North of the Thrust.
LLANDEILO.	Hen-dy-Capel Mudstones. (Zone of <i>Nemagraptus gracilis</i> .)
LLANVIRN.	Benar Beds. (Zone of <i>Didymograptus extensus</i> ?) Probable unconformity.
Llanengan Mudstones. } Tudwal Sandstones and } Grits. } (Zone of <i>Didymograptus extensus</i> .)	ARENIG.
Great unconformity.	TREMADOC. Abersoch Beds.
Ffestiniog Beds. (Only in East St. Tudwal's Island.)	DOLGELLY. FFESTINIOG.
Maentwrog Beds. Probable unconformity.	MAENTWROG.
Nant-pig Mudstones. Caered Mudstones and Flags.	MENEVIAN (of Merionethshire).
Cilan Grits. Mulfran or Manganese Beds. Hell's Mouth Grits.	HARLECH GRITS (of Merionethshire) (in part).
Base not seen.	

Pisolitic iron-ore is well developed in the district, and occurs chiefly in the Llandeilo Beds along the line of the overthrust; it is regarded as of sedimentary origin. The glacial geology is only briefly dealt with; but evidence is presented to show that, during the last phase of glaciation, the ice was moving across the peninsula in a westerly direction out of Cardigan Bay.

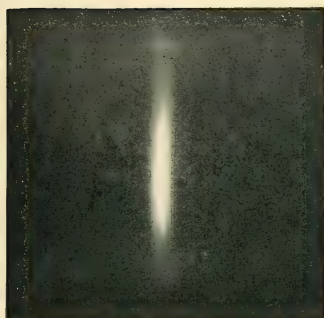


FIG. 1.



FIG. 2.

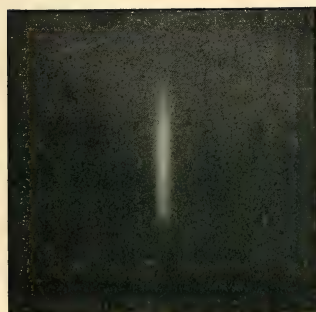


FIG. 3.



FIG. 4.







FIG. 1.

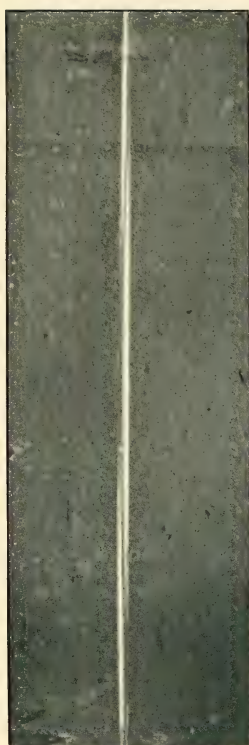
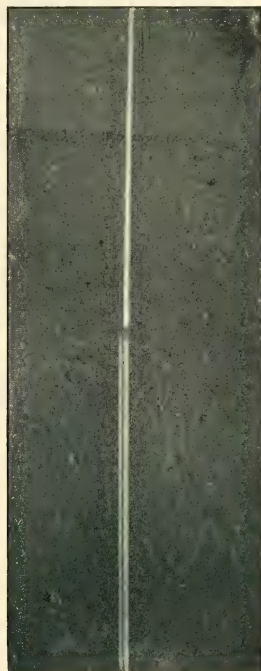


FIG. 2.



$D_1 D_2$   
FIG. 3.

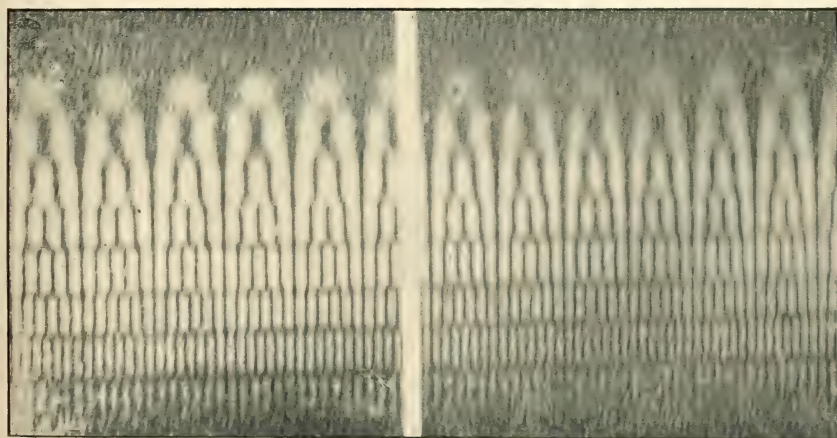


FIG. 4.



THE  
LONDON, EDINBURGH AND DUBLIN  
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AND  
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

APRIL 1914.

LXIV. *The High-frequency Spectra of the Elements, and the Structure of the Atom.* By J. W. NICHOLSON, M.A., D.Sc., *Professor of Mathematics in the University of London*\*.

IN the Philosophical Magazine for December last, Mr. H. G. J. Moseley has described some experiments which give a new order of simplicity to the determination of wavelengths of the characteristic X-radiation emitted from metals, —a determination which, when performed with sufficient completeness, supplies perhaps the most hopeful way of obtaining a more intimate knowledge of the inner structure of the atom, and of the essential relations between the various elements. The results of the experiments are remarkable, and indicate a definite law which appears to connect successive elements in the Periodic Table. But at the same time, the particular interpretation of these results which has been suggested appears to the writer to be very unsatisfactory, and in calling attention to some points of theory which have been overlooked, not only in this interpretation but also almost universally in recent work on the possible nature of atoms, an opportunity is afforded of scrutinising, in a general way, some of the fundamental assumptions involved in such work, restricting attention, however, only to certain special points on which erroneous conclusions have been founded.

A very attractive theory as to the nature of series spectra has been put forward recently by Dr. Bohr †, and it has been

\* Communicated by the Author.

† Phil. Mag. July and Sept. 1913.



supposed\* that his formula for spectra, applied to the steady states of an inner ring of four electrons rotating round a nucleus whose charge corresponds to the "atomic number" of the element, will account for the principal line found by Moseley in the X-ray spectra of the elements from calcium to zinc in the Periodic Table. The present paper is in no way intended as a criticism of Bohr's theory of the origin of spectra in general, and of the hydrogen and helium spectra in particular, but it puts forward the view that this particular application of the theory cannot be made in the manner contemplated, without a serious conflict with the recent results obtained by Rutherford, Barkla, and others as to the number of electrons in atoms, which seem to indicate that the number is about half the atomic weight.

Recently there has been a striking change of opinion as to the inner significance of the Periodic arrangement of the elements. It is now largely believed that the position of an element is not determined by its atomic weight so much as by its "atomic number"—defined as the electron-equivalent of the positive nucleus of the atom. This view appears to be due originally to van den Broek†, and will be referred to as van den Broek's hypothesis. It has been developed by Soddy and others, and appears to throw a light upon the true positions of the elements of the rare-earth group and the radioactive products. For, according to this hypothesis, several elements may occupy the same position in the Periodic Table, provided that they possess nuclei with equal charges, but different arrangements of electrons circulating round the nuclei in possible steady motions, and slightly different atomic weights, so that the number which defines the atomic weight as found in the laboratory is actually the mean value of a set of numbers each corresponding to a more or less stable variety of the element. There is some evidence for the truth of this view, for it seems that the spectra of two elements different in their degree of activity may be identical, as the investigation of Rossi and Russell‡ on the spectrum of ionium tends to show.

But to admit that there is truth, in a general way, in van den Broek's hypothesis, does not of necessity contain the further admission that the atomic number of an element corresponds *exactly* to its position in the Table as we now know it. It is still possible, for example, to take the view that other elements may exist between hydrogen and lithium, in addition to helium; and if an element like potassium is

\* Moseley, *Phil. Mag.* Dec. 1913.

† *Phys. Zeit.* xiv. p. 32 (1913).

‡ *Roy. Soc. Proc. A.* lxxxvii, p. 478 (1912).

radioactive, giving  $\alpha$  particles with a smaller velocity of ejection than usual, some place may have to be found for unstable elements of lower atomic weight. In any case, van den Broek's hypothesis involves, in its present form, the supposition that the atomic numbers of lithium, beryllium, and boron are three, four, and five respectively, and in this paper we shall find that, on Bohr's theory of the constitution of atoms more complex than helium at least, this cannot be reconciled with theoretical considerations. If we are to retain Bohr's theory of such complex atoms, that theory must give up van den Broek's hypothesis in its present form, and substitute a modified hypothesis. This portion of Bohr's theory, however, is admittedly of a more tentative form, and is only precise for the two simplest elements, hydrogen and helium, which do not come within the scope of this paper. The need for modification of van den Broek's hypothesis, pointed out in the paper, therefore does not bear upon Bohr's *spectral* theory in any way, or even to a great extent on his theoretical reason for the existence of Rydberg's universal constant in all spectra.

It must be pointed out that the necessity for the abandonment of van den Broek's hypothesis in its present form, and the substitution of a similar form which allows the atomic number to be different from the position in the Periodic Table, is solely determined by the portions of Bohr's theory which are not related to the hypothesis, for example, the specification of the equal and constant angular momenta of all electrons in the atom, and the mode of determination of the probable valency of an element, based on the supposition that the readiness of an atom to take up an electron and form a new charged configuration may be determined from a consideration of the total energies which should be applied to the configurations in order to scatter their component parts to an infinite distance from each other. It may be that either of these procedures is incorrect. As regards the first, for example, the only definite cases worked out by Bohr, in so far as spectra are concerned, are those of hydrogen and helium with *only one electron*. In these cases, it is essential to suppose that the angular momentum of the electron is  $h/2\pi$ , where  $h$  is Planck's constant; but in the presence of other electrons, this relation to  $h$  may be modified and come to depend on the number of electrons.

There are indications that this modification is necessary. For example, if the angular momentum of each electron in the neutral helium atom is  $h/2\pi$ , we cannot obtain the ordinary helium spectrum, as a future paper will show. Moreover, in systems with a *simple* nucleus, this modification

is certainly necessary\*, and it will probably remain so when the nucleus is, as is probable in terrestrial elements, of a complex character. Our precise conclusion will be, therefore, that we cannot retain Bohr's theory of the *more complex* atoms, and van den Broek's hypothesis in its present form, simultaneously, and one or the other must be changed or abandoned altogether. In the two cases of hydrogen and helium there is no conflict, however.

It has been assumed universally that an atom can form a Saturnian system with concentric rings of electrons rotating round a positive nucleus, and this assumption is an important part, for example, of the later sections of Bohr's theory which do not deal with spectra, but rather with the chemical properties of atoms. The phenomena of radioactivity have led inevitably to the conclusion that an atom with a simple nucleus, or pure positive charge, at its centre, and a single ring of rotating electrons, is insufficient for their interpretation, although the measurements of scattering of  $\alpha$  and  $\beta$  particles have compelled Rutherford to enunciate the view that the atom is Saturnian. We are obliged, therefore, to imagine a more complicated arrangement. For it now seems certain that the  $\beta$  particles in radioactive transformations cannot come from a ring whose radius is comparable with the atomic radius, and accordingly they must come either from an inner ring, or from the nucleus itself. The attempt to preserve the simple character of the nucleus, and the reluctance to endow it with a structure of its own, have led to the fairly general adoption of the view that the  $\beta$  particles come from an inner ring of electrons, which can also give rise to radiation of the appropriate wave-length for  $\bar{X}$ -rays, just as an outer ring is believed to give rise to the visible spectrum of an element.

A mathematical examination does not confirm the possibility of such an arrangement. We shall consider the question, in the main, from a point of view which is common to ordinary dynamical theory and to that of Bohr, which is the first non-mechanistic theory yet given. Bohr has supposed that in the determination of the *steady states* of rotation of an atomic system, the ordinary mechanics can be used, proceeding according to the law of inverse square for both the repulsion between electrons and the attraction between an electron and the nucleus. The formula so obtained for circular motion may be written, for a single ring of  $n$  electrons rotating round a nucleus  $Ne$  with angular velocity  $\omega$ ,

$$\omega^2 = \frac{e^2}{ma^3} (N - \frac{1}{4} S_n),$$

\* Monthly Notices of R. A. S. July 1912 and later.



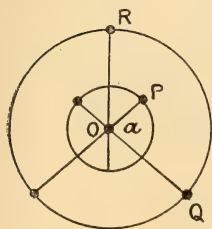
where  $a$  is the radius of the ring,  $m$  the mass of an electron of charge  $e$ , and

$$S_n = \sum_{r=1}^{r=n} \operatorname{cosec} \frac{r\pi}{n}.$$

This formula is vital to his theory of the Balmer series of the hydrogen spectrum, and any departure from these particular correspondences with ordinary dynamics, and from the ordinary ideas of force, such as a change in the law of force in the neighbourhood of the nucleus, would invalidate the theory. The ordinary dynamics is thus essential up to a point, and beyond that point, for the present purpose, it is not necessary to go. Although the additional specification of the constancy of angular momentum is required—only in the sense that some additional specification, though not necessarily this particular one, is required,—in order to make the atom definite, it cannot be used alone, without the dynamical equation which gives the angular velocity as a function of the radius.

We may now consider the possibility of two rings, of radii  $a$  and  $b$ , rotating round a nucleus of any strength  $Ne$  with a common angular velocity  $\omega$  in the same plane. This case cannot occur in Bohr's theory, but it can in the ordinary theory, and it is not possible to dismiss it as non-existent *a priori*, for the effect of one ring on the other varies very much with the number of electrons in the rings. Thus, for example, if we take two electrons in each ring, symmetrically situated so that the line joining the inner pair, passing through the nucleus, is perpendicular to the corresponding line joining the outer pair, then the electrons of the inner ring tend to expand the outer into a larger radius, and *vice versa*. On the other hand, in the case dealt with below in more detail, where there are three electrons in each ring, the inner ring again tends to expand the outer, but the outer tends to contract the inner.

Taking first, therefore, a special case, we select that shown



electron opposite to it in the outer ring, and since

$$PQ^2 = a^2 - ab + b^2,$$



we find that the resultant force on P due to Q and R is

$$e^2(b-2a)/(a^2+b^2-ab)^{\frac{3}{2}},$$

along PO, towards O. The equation of steady motion of P is therefore

$$\frac{m a \omega^2}{e^2} = \left(N - \frac{1}{\sqrt{3}}\right) \frac{1}{a^2} - \frac{1}{(a+b)^2} + \frac{b-2a}{(a^2+b^2-ab)^{\frac{3}{2}}},$$

where the term with  $\sqrt{3}$  is the ordinary effect of the other electrons in the same ring as P. The equation for Q is similarly

$$\frac{m b \omega^2}{e^2} = \left(N - \frac{1}{\sqrt{3}}\right) \frac{1}{b^2} - \frac{1}{(a+b)^2} + \frac{a-2b}{(a^2+b^2-ab)^{\frac{3}{2}}}.$$

If  $b/a = x$ , we find that  $x$  is a root of the equation

$$\left(N - \frac{1}{\sqrt{3}}\right) \left(1 - \frac{1}{x^3}\right) + \frac{x^2-1}{x(1-x+x^2)^{\frac{3}{2}}} = (1+x)^{-2} \left(1 - \frac{1}{x}\right),$$

$x=1$  is a root, and all others are given by

$$\left(\frac{1}{1+x}\right)^2 = \left(N - \frac{1}{\sqrt{3}}\right) \frac{1+x+x^2}{x^2} + \frac{x+1}{(1-x+x^2)^{\frac{3}{2}}},$$

which has no real positive roots, whatever integer is put for N. The only solution is therefore  $b=a$ , so that all the electrons are in the same ring. For attractive forces between the electrons, on the other hand, there would be another solution, even for this small number of electrons,—suggesting that the essential difference between atomic problems and the phenomena of Saturn's rings depends on the change of sign in the force, which is actually the reason for the difference, from one point of view.

A large number of apparently possible systems of two rings may be shown to lead to the same conclusions, and, in fact, a very general proof can be given. We may, however, at this point, give only an approximate treatment of the general case in which the radii are presumed to be widely different, for this is the case usually quoted. Let there be  $n$  and  $m$  electrons in the inner and outer rings respectively of a neutral atom, so that  $N=n+m$ . Then if  $a$  is very small in comparison with  $b$ , so that the influence of the outer ring on the inner is small, we may write

$$\omega^2 = \frac{e^2}{m a^3} \left(N - \frac{1}{4} S_n\right)$$

$$\omega^2 = \frac{e^2}{m b^3} \left(N - n - \frac{1}{4} S_m\right),$$

since the outer is practically under the influence of a nucleus  $N - n$  or  $m$ . Thus

$$a^3/b^3 = (N - \frac{1}{4} S_n)/(m - \frac{1}{4} S_m),$$

and  $a$  and  $b$  must be comparable in all cases, in contradiction to the fundamental assumption.

The above relates, of course, to rings moving with the same angular velocity, for which case a somewhat cursory treatment is possible. When they have different angular velocities, the electrons of the two rings are not in the same configuration relatively to each other at two successive instants, and their orbits cannot in such circumstances remain circular. Before proceeding further with such a case, therefore, we must make a definite choice between the older electrodynamics and a non-mechanistic theory such as that of Bohr, at variance with ordinary electrodynamics, and the method of argument adopted must depend on this choice.

Let us choose, in the first place, the ordinary electrodynamics. We are then compelled to suppose that an electron in accelerated motion must radiate energy, and an atom containing a system of circulating electrons would rapidly lose its internal energy unless the radiations from all the electrons could be arranged so as to interfere. Schott has proved conclusively that this condition requires all the electrons to be arranged at every specified instant on circles with a common axis, though their orbits are not necessarily circular, the circles on which they are arranged being capable of varying from one instant to another. A set of orbits satisfying this condition, which at the same time are not circular orbits, is mentioned later in this paper, and other sets exist, illustrated, for example, by the remarkable epitrochoidal orbits discussed by Schott\*, which could, so far as the necessary interference of radiation is concerned, almost be described as the steady motion in an atom, under the influence of a nucleus, though the interference is in this case probably too imperfect.

"Steady motion" is a term normally applied to dynamical systems, all of whose component parts move with constant velocities. But such a term can be applied to the motions in an atom, if they are really periodic, and if they involve no radiation of energy,—if in fact, on the older electrodynamics, Larmor's condition, that the vector sum of the accelerations of all the electrons is permanently zero, is fulfilled. As we have seen, the non-mechanistic theory of Bohr uses ordinary dynamics to obtain the condition of steady motion or dynamical

\* 'Electromagnetic Radiation,' Camb. Univ. Press, 1911.

equilibrium, all the electrons in any ring having the same velocity, and a normal acceleration  $a\omega^2$ , to which Newton's Second Law is applied. When there are two rings, the particles cease to move in a circle, and we can see at once that no dynamical equilibrium with a constant velocity for each electron can exist consistent with the principle of universal constancy of angular momentum per electron, unless every electron is describing a circle, whether the angular momenta and velocities of every electron are the same or not. For it would involve, for any electron, of polar coordinates  $(r, \theta)$ , where A and B are constants,

$$\left(\frac{dr}{dt}\right)^2 + r^2\dot{\theta}^2 = A^2, \quad r^2\dot{\theta} = B,$$

or

$$\dot{r}^2 + \frac{B^2}{r^2} = A^2, \quad t + \text{Const.} = \int \frac{rdr}{\sqrt{A^2r^2 - B^2}},$$

unless  $r = B/A$ , a special solution, and finally

$$r^2A^2 = B^2 + A^2(t + \text{Const.})^2,$$

so that the electron must proceed to infinity. But a non-circular path, permanently described with constant angular momentum in an atom, with variable velocity, may always be regarded as part of a steady state, according to Bohr's theory, where the consequent radiation does not have the value calculated by the ordinary electrodynamics as corresponding to accelerated motion.

Returning to the ordinary electrodynamics, the only solutions of the general problem of orbits which can be obtained, subject to the condition of interference of radiation or the equivalent condition of a zero vector sum of accelerations, require that the electrons shall be arranged at every instant on circles coaxial with each other, as proved by Schott. Two coplanar rings could satisfy this condition, but it would involve further a regularly preserved phase relation among the electrons in each circle, and between the two circles. We must imagine that the electrons in any one ring are all equidistant from the nucleus at any instant, and if the rings are rotating with different angular velocities, the electrons cannot be distributed round their rings at equal angular intervals, but must be oscillating tangentially in relation to the general motion of the ring.

Apart from the improbability of such phase relations being preserved—for it cannot be conclusively proved that they are impossible in all cases,—there is a decisive way of settling



the question of the existence of such coplanar rings. For if the rings, with these particular phase relations between their component electrons, have no existence when the numbers of electrons are small, they cannot exist at all for a finite number of electrons. The restrictions on their motion, with a large number of electrons, must be at least as difficult to satisfy as in the simpler cases, until we arrive at such a number of electrons in each ring that it can be regarded as a continuous distribution. It is easy to prove, although the mathematical treatment is not given here, that we cannot obtain motions of two coplanar rings at all, in which the electrons of each ring are on a circle at any instant, for the cases of two or three electrons. In fact, it is fairly obvious that the only solution is the case of an infinite number of electrons in each ring, so that the rings form continuous distributions and are perfectly symmetrical. In no other case can we have the electrons on circles at any instant in the same plane.

Coplanar rings are therefore impossible in a permanent atom constructed on the basis of the ordinary electrodynamics, and an atomic theory can only depend on them in so far as it departs from this dynamics. The only atomic theory yet proposed, which does not proceed according to such dynamics, and at the same time requires coplanar rings in its present form, is that of Bohr. In substance, this theory involves the assumption that if two rings have very different radii, and one rotates much more rapidly than the other, an electron of either ring rapidly passes through all possible positions relatively to the other ring, so that each ring can be regarded, in its effect on the other, as a uniform electrical distribution, provided that the number of electrons concerned is moderately large.

Bohr\*, however, definitely states that this is an assumption made provisionally, for he only points out that the orbits *may* remain approximately circular in such cases. Yet it is significant that the radii of the orbits in his lithium atom work out only in the ratio of about 3 to 1, which does not suggest that the cumulative effect of the outer electron on the two inner ones is likely *a priori* to introduce small periodic variations from a circular orbit. The mathematical difficulties of testing such an assumption are, of course, very great in any case with much generality, but there is at least one case for which analysis may be found readily—the suggestion he makes as to the nature of a lithium atom. The question at issue is: Are the deviations from circular motion of a

\* Phil. Mag. Sept. 1913, p. 481.



periodic character or cumulative? If they are cumulative, we can discover the fact by treating them as small, and finding that they actually are large, somewhat after the usual manner of testing the stability of a system, although of course in this case the problem is not one of stability, but of the ordinary "steady motion" of the atom, not involving any radiation of energy.

It would not be logical, on any view, to apply Newton's Second Law only to the circular steady state, and not to any other. If the component of radial force is equal to the mass-acceleration in the one case, as is necessary for Bohr's spectral formula, it must be also in the other. Bohr's only deviation from ordinary dynamics, apart from the quantum-character of the radiation, occurs in relation to the component acceleration of an electron in its plane, transverse to the line joining it to the nucleus,—the equation for which is replaced by the law of constancy of angular momentum. The necessity for this law seems to point to something in the nature of a tube of force, constituting the mechanism of "binding," which compels the tube to have a definite angular momentum in the plane of the ring, but not a definite length, for the electron at the end takes up the corresponding position determined by the forces and Newton's law, as Bohr assumes throughout his paper. Transverse to the plane, also, Newton's law can be used even for vibrations.

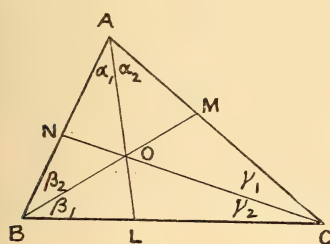
### *The Atom of Lithium.*

The configuration for the atom of lithium, suggested by Bohr's theory, consists of a ring, approximately circular, of two electrons rotating round a nucleus  $3e$ , with a solitary or valency electron outside. Bohr chooses this configuration in spite of the fact that the collection together of a single ring of three electrons would correspond to a greater emission of energy, on his mode of calculation. The chemical valency of lithium is definitely unity, and the system at first sight is very attractive. We must examine the deviations of the orbits from the circular form, in order to ascertain whether the system can be permanent. Bohr's method of treatment, by which his approximations are obtained, would evidently fail if the deviations were cumulative. If they are small, the substitution of a *uniformly* electrified ring for a ring of electrons will give a very accurate idea of the effect of one ring on another, and in fact an examination of Bohr's Table\*, which the writer has made, shows that it gives surprisingly

\* *L. c.* p. 485.

accurate results. But the use of such a method, introducing a uniformity round the ring which does not actually exist, must necessarily cover up any cumulative character in the deviations from a circular orbit, so that a rigorous examination is necessary in at least one case. For although two uniformly electrified rings can obviously, by virtue of symmetry, rotate permanently with different angular velocities round a nucleus, the same thing is not obvious for rings such as those of Bohr, containing 8 electrons at the most.

We accordingly take up the general problem of steady orbits of three electrons, moving about a nucleus  $Ne$  with specified angular momentum, but otherwise subject to Newton's law. Let the electrons be situated at any instant at the angular points of a triangle  $ABC$ , of sides  $(a, b, c)$ , the nucleus being at an internal point  $O$ , distant  $(r_1, r_2, r_3)$  from the electrons.



The constancy of the angular momentum of any electron implies that the electrostatic force on it during its steady orbit must be in the radius vector to the nucleus. Bohr uses these electrostatic forces throughout his papers, his deviation from ordinary dynamics being, as we have seen, equivalent to the supposition

that *the tube of force, or some other agency, constrains the electron to move so that it experiences no force transverse to the tube in the plane of the ring*, force being interpreted, in this statement, as non-electrostatic force. This is the formal mathematical description of the nature of "binding."

In addition, a balance must be obtained between the electrostatic forces and the centrifugal or other accelerations. For any one of the three electrons, therefore, the resultant electrostatic force is along the radius vector to  $O$ , and the forces between electrons being given by the inverse square law, we have

$$\frac{\sin \alpha_1}{c^2} = \frac{\sin \alpha_2}{b^2}, \quad \frac{\sin \beta_1}{a^2} = \frac{\sin \beta_2}{c^2}, \quad \frac{\sin \gamma_1}{b^2} = \frac{\sin \gamma_2}{a^2},$$

the angles being shown in the figure. If the radii vectores meet the sides of the triangle in  $L, M, N$ , these conditions are equivalent to

$$\frac{BL}{LC} = \frac{c^3}{b^3}, \quad \frac{CM}{MA} = \frac{a^3}{c^3}, \quad \frac{AN}{NB} = \frac{b^3}{a^3}.$$

The point O can satisfy these three conditions simultaneously for any triangle, for they are in accord with Ceva's theorem

$$BL \cdot CM \cdot AN = LC \cdot MA \cdot NB$$

relating to concurrent lines through the angular points of a triangle.

Thus other than circular orbits may exist for three particles moving with specified angular momenta about a nucleus, and the condition of angular momentum alone does not greatly restrict the orbits. We can express the radii to the electrons in terms of  $(a, b, c)$  as variables at any instant, for

$$\frac{BL}{c^3} = \frac{LC}{b^3} = \frac{a}{b^3 + c^3},$$

and therefore

$$(BL, LC) = (ac^3, ab^3)/(b^3 + c^3)$$

$$(CM, MA) = (ba^3, bc^3)/(a^3 + c^3)$$

$$(AN, NB) = (cb^3, ca^3)/(a^3 + b^3),$$

$$AL = (c^2 + BL^2 - 2c BL \cos B)^{\frac{1}{2}}$$

$$= \frac{bc}{b^3 + c^3} \{ (b + c)(b^3 + c^3) - bc a^2 \}^{\frac{1}{2}},$$

and we can easily derive

$$OA = r_1 = \frac{bc}{a^3 + b^3 + c^3} \{ (b + c)(b^3 + c^3) - bc a^2 \}^{\frac{1}{2}} \quad (1)$$

with two cyclic expressions for  $r_2$  and  $r_3$ , so that the atom is at any instant completely expressed in terms of the distances between the electrons. In obtaining these formulæ, we have supposed, on the one hand, that the nucleus is at rest, on account of its great inertia, but on the other hand, only that the angular momenta of the electrons are constant,—not necessarily equal, as in Bohr's theory.

Consider now the force tending to increase OA. The attraction of the nucleus on the electron A is  $Ne^2/OA^2$ , and the resolved part of the electronic repulsions is

$$e^2 \left( \frac{\cos \alpha_1}{c^2} + \frac{\cos \alpha_2}{b^2} \right),$$

which, after considerable reduction, becomes

$$e^2 OA (a^3 + b^3 + c^3)/b^3 c^3 \dots \dots \dots (2)$$

If  $r_1 = OA$ , the steady orbit of the first electron A is given,

after the usual manner of central orbits, by

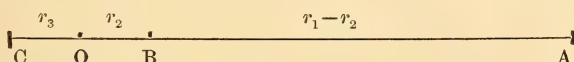
$$\frac{d^2 u_1}{d\theta_1^2} + u_1 = \frac{e^2}{mh_1^2} \left( N - \frac{r_1^3}{b^3 c^3} (a^3 + b^3 + c^3) \right), \quad . \quad . \quad (3)$$

where  $u_1 = 1/r_1$ ,  $mh_1$  is the angular momentum of the electron, and there are similar equations for the other two orbits.

These equations cannot be accurately solved in general terms unless the triangle ABC is at every instant equilateral,—this does not include only circular motion. We shall return to these equations later. Without solving them at all, we may show more simply that Bohr's lithium atom is not a possible configuration.

In that atom, the two inner electrons rotate several times faster than the outer one, so that positions must arise frequently in which the three electrons are in a straight line, and the mutual repulsions between the electrons then act along this line. The only other forces being the attractions of the nucleus, which are radial, we see that when the electrons are in a line, this line must pass through the nucleus. Otherwise the conservation of angular momentum for each electron is destroyed by electrostatic forces, which Bohr recognizes as causing accelerations.

When the electrons are in this configuration, let the instantaneous values of the radii of their orbits be  $(r_1, r_2, r_3)$ , shown on the figure, where (A, B, C) are the electrons, and



O is the nucleus. On Bohr's theory,  $r_2$  and  $r_3$  will be nearly equal, and  $r_1$  much larger than either ( $r_1 = 3r_2$  approximately). The sides of the triangle are

$$a = r_2 + r_3, \quad b = r_1 + r_3, \quad c = r_1 - r_2,$$

and  $a = b - c$ , as the triangle is instantaneously a straight line. Since  $(r_1, r_2, r_3)$  are determined already in terms of  $(a, b, c)$  by the condition of angular momentum, we can in this case find an identical relation between the radii. Thus since  $a = b - c$ ,

$$\left. \begin{aligned} r_1 &= \frac{bc}{a^3 + b^3 + c^3} \{ (b+c)(b^3 + c^3) - bca^2 \}^{\frac{1}{2}} = \frac{bc(b^2 + c^2)}{a^3 + b^3 + c^3} \\ r_2 &= \frac{ca}{a^3 + b^3 + c^3} \{ (c+a)(c^3 + a^3) - cab^2 \}^{\frac{1}{2}} = \pm \frac{abc(c-a)}{a^3 + b^3 + c^3} \\ r_3 &= \frac{ab}{a^3 + b^3 + c^3} \{ (a+b)(a^3 + b^3) - abc^2 \}^{\frac{1}{2}} = \frac{ab(a^2 + b^2)}{a^3 + b^3 + c^3} \end{aligned} \right\} \quad (4)$$

$$\text{and therefore} \quad \frac{ar_1}{b^2 + c^2} = \pm \frac{br_2}{c^2 - a^2} = \frac{cr_3}{a^2 + b^2} \quad . \quad . \quad . \quad (5)$$



The ambiguity of sign is necessary for the inclusion of all possible cases in which ( $r_1, r_2, r_3$ ) may be positive. Taking first the negative sign in the ambiguity, we can deduce at once

$$ar_1 + br_2 = cr_3,$$

$$\text{or} \quad r_1(r_2 + r_3) + r_2(r_1 + r_3) = r_3(r_1 - r_2),$$

$$\text{or} \quad r_1(r_2 + r_3) = 0,$$

which can only be true for positive values if  $r_1 = 0$ , or the outer electron is in the nucleus. Then, of course, we have only two electrons, and a solution obviously exists with  $r_2 = r_3$ . We are compelled, therefore, to take the positive sign in the ambiguity, and

$$\frac{ar_1}{b^2 + c^2} = \frac{br_2}{c^2 - a^2} = \frac{cr^3}{a^2 + b^2}.$$

Each ratio is equal to  $(ar_1 - br_2)/(a^2 + b^2)$ , so that

$$ar_1 - br_2 = cr_3$$

$$\text{or} \quad r_1(r_2 + r_3) - r_2(r_1 + r_3) = r_3(r_1 - r_2),$$

which is an *identity*. The two equations involved in (5) are therefore equivalent only to one, namely,

$$r_2(a^2 + b^2) = cr_3(c - a),$$

or in terms only of radii

$$r_2^3 + r_1^2(r_2 - r_3) + r_3^2(r_1 + r_2) + 5r_1r_2r_3 = 0, \quad \dots \quad (6)$$

and the whole set of equations are equivalent to this and

$$r_1 = \frac{bc(b^2 + c^2)}{a^3 + b^3 + c^3} = \frac{c(b^2 + c^2)}{a^2 + b^2 + c^2 - ac}$$

since  $b = a + c$ . This becomes, in terms of radii,

$$r_1(a^2 - ca) = (c - r_1)(b^2 + c^2)$$

$$\text{or} \quad ar_1(a - c) = -r_2(b^2 + c^2),$$

and finally

$$r_2^3 + r_1^2(r_2 - r_3) + r_3^2(r_1 + r_2) + 5r_1r_2r_3 = 0,$$

which is not distinct from (6).

Thus all the equations are only equivalent to this single equation, which must always hold between the instantaneous radii of the orbits when the three electrons are in a straight line. If  $r_2$  and  $r_3$  are nearly equal, and not zero, we find

$$6r_1 + 2r_2 = 0$$

which cannot be satisfied by any positive value of  $r_1$ .

Thus three particles under the inverse square law of repulsion cannot, whatever be the attraction of the nucleus, have steady orbits round it with constant angular momenta, even if these angular momenta are unequal, where two of them are approximately describing the same circle with a different angular velocity from the third, and Bohr's lithium atom fails.

It seems probable, in fact certain, that the other atomic configurations with coplanar rings must fail also. If at any instant, the two inner lithium electrons were arranged so as to describe approximately the same circle with any possible arrangement of angular velocities, the subsequent deviations from that circle would accumulate and become large. This can be proved independently, but it is not thought necessary to give the proof here.

We can, however, go further with the present investigation, and find how nearly it is possible for the two inner electrons to rotate in the same ring.

Let  $\alpha$  be the radius of the circle to which their orbits most nearly approach, and write  $r_2 = \alpha(1-u)$ ,  $r_3 = \alpha(1+u)$ , where  $u$  is essentially between 1 and  $-1$ . Then the identical relation becomes

$$\alpha^2(1-u)^3 - 2r_1^2u + \alpha(1+u)^2(r_1 + \alpha - \alpha u) + 5\alpha r_1(1-u^2) = 0,$$

or if  $r_1/\alpha = \rho$ ,

$$f(u, \rho) \equiv -u\rho^2 + (3-2u)(1+u)\rho + (1-u)(1+u^2) = 0. \quad (7)$$

This equation gives  $u$ , expressing the divergence of the inner electrons from a circular orbit, as a function of  $\rho$ , the ratio of the mean radii of the two rings.

$u$  will be a minimum for a value of  $\rho$  satisfying  $\frac{du}{d\rho} = 0$ .

$$\text{But} \quad \frac{\partial f}{\partial \rho} + \frac{\partial f}{\partial u} \frac{du}{d\rho} = 0,$$

and as  $\partial f/\partial u$  must be finite, we may write  $\partial f/\partial \rho = 0$  instead, whence

$$-2u\rho + (3-2u)(1+u) = 0. \quad \dots \quad (8)$$

The possible minimum values of  $u$  satisfy (7) and (8), and therefore eliminating  $\rho$ ,

$$(3-2u)^2(1+u)^2 = -4u(1-u)(1+u^2)$$

which reduces to the quadratic

$$15u^2 - 10u - 9 = 0$$

$$\text{and} \quad u = 0.90784 \quad \text{or} \quad -0.24117,$$

to which correspond by (8),

$$\rho = 0.657 \quad \text{or} \quad -6.479.$$

Again,  $d^2u/d\rho^2$  must be positive for a minimum, and we find

$$\frac{\partial^2 f}{\partial \rho^2} + \frac{2\partial^2 f}{\partial \rho \partial u} \frac{du}{d\rho} + \frac{\partial^2 f}{\partial u^2} \left(\frac{du}{d\rho}\right)^2 + \frac{\partial f}{\partial u} \frac{d^2u}{d\rho^2} = 0,$$

and as  $du/d\rho = 0$ ,

$$\begin{aligned} \frac{d^2u}{d\rho^2} &= - \frac{\partial^2 f}{\partial \rho^2} / \frac{\partial f}{\partial u} \\ &= - \frac{4u^3}{9+5u} \end{aligned}$$

after some reduction. For a minimum of  $u$ , this should be positive, and therefore the first value of  $u$  gives no minimum. The second value gives  $r_1$  negative and is inadmissible.

Finally, therefore, there is no minimum of  $u$  as  $\rho$  ranges from unity, its smallest value, to infinity. Nor is there a maximum between these limits, for  $\rho$  is less than unity with the first value of  $u$ , in contradiction to the hypothesis that  $r_2$  and  $r_3$  were the two radii for the *inner electrons*. Thus the divergencies from circular orbits must increase *continuously* as the outer electron is nearer and nearer to the atom; and it is never possible to regard the two electrons nearer the nucleus as forming a ring.

In fact, in Bohr's atom,  $\rho$  is about equal to 3, the ratio of the two radii of the circles to which the orbits most nearly approach. Thus  $u$  is given by the cubic

$$-9u + 3(3-2u)(1+u) + (1-u)(1+u^2) = 0$$

or

$$u^3 + 5u^2 + 7u - 10 = 0$$

whose real root is about  $u=0.85$ . Thus the radii of the orbits of Bohr's inner electrons, in the permanent state of the atom, should be in the ratio  $(1.85)/(0.15)$  or 12 to 1 when the electrons are in a straight line.

It is easy to verify this mode of reasoning in a variety of ways. Thus if  $u=1$ , signifying  $r_2=0$ ,  $r_3=2\alpha$ , where one inner electron is in the nucleus, then (7) gives  $\rho^2=4$  or 0, so that  $r_1=0$  or  $2\alpha$ . Thus there is only one electron in the atom, or there are two, equidistant from the nucleus.

A similar process can be applied to the model atoms of beryllium and boron treated by Bohr, and leave little doubt that coplanar rings of electrons are as impossible on his theory as on the ordinary theory. In fact, in order to retain them at all, we must depart from the ordinary dynamics even more completely, and admit the possibility of an uncompensated force of *electrostatic* type producing no corresponding

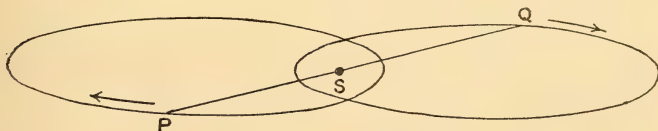
acceleration, or else change the laws of force between electrons altogether, while preserving the law between electron and nucleus.

*Electronic arrangements in an Atom.*

It follows from the preceding considerations that if the more complex atoms have the number of electrons which, from the results of experiments on scattering, seem necessary, these electrons must either form a single ring, or rings in parallel planes. This does not imply that those of any single ring actually move in a circle. Accepting Bohr's view that the dynamical equilibrium of an electron in the atom, while involving an acceleration, centrifugal or other, does not involve a consequent radiation, we can make the orbits elliptical. Returning, for example, to the equation for the orbits of three electrons about a nucleus, let us suppose that they remain at the corners of a variable equilateral triangle. Then any orbit is given by

$$\frac{d^2u_1}{d\theta_1^2} + u_1 = \frac{e^2}{mh_1^2} \left( N - \frac{1}{\sqrt{3}} \right)$$

and its most general form is an ellipse, if the electron remains in the atom. Imagine, more generally, a system of  $n$  electrons describing a set of equal ellipses, with a common focus at which the nucleus is situated, and with their successive major axes inclined at equal angles  $2\pi/n$  to each other. If the electrons are at corresponding points at any instant, they are at the corners of a regular polygon inscribed in a circle. Thus at any single moment they form a ring, and even on the older electrodynamics, such a system has little radiation, for the vector sum of the accelerations is zero if there is more



than one electron. The figure shows the case of two electrons  $P$  and  $Q$ . In the general case, if  $r$  is the instantaneous distance of an electron from the nucleus, the radial force on it is

$$-\frac{e^2}{r^2} \left( N - \frac{1}{4} S_n \right)$$

where  $S_n = \sum_1^{n-1} \operatorname{cosec} \frac{r\pi}{n}$ ,



and its orbit is given by

$$\ddot{r} - r\dot{\theta}^2 = -\frac{e^2}{mr^2}\left(N - \frac{1}{4}S_n\right), \quad r^2\dot{\theta} = \text{Const.},$$

which leads as usual to the ellipse. If  $a$  is the semi-axis major of any orbit, the mean angular velocity  $\omega$  satisfies

$$\omega^2 = \frac{e^2}{ma^3}\left(N - \frac{1}{4}S_n\right),$$

as in a circular orbit of radius  $a$ .

When a circular orbit ceases to be stable, as in Bohr's theory when  $n$  is greater than 8, there may be stable sets of elliptic orbits, and if there are to be many electrons in the atom, this is a probable configuration; though perhaps a more probable one consists of parallel rings, or even parallel arrangements describing elliptic orbits.

Returning to the lithium atom, we see that, since an inner *ring* of two electrons is not possible, the attempt to treat the atom from a point of view which assumes that the outer part of the atom contains a number of electrons equal to the normal valency of the element, breaks down. For there seems to be no method of disposing of one electron in order to endow it with peculiar properties. For lithium, there are presumed to be three electrons, and no arrangement not in one plane can satisfy Bohr's conditions. Yet the only coplanar arrangement is that of a single ring. We must accept one of two alternatives. Either the number of electrons most remote from the nucleus does not represent the chemical valency, as has been generally supposed, except by Bohr, or the lithium atom does not contain 3 electrons. To accept the second alternative gives up van den Broek's hypothesis in its present form.

Bohr rejects the first alternative, as for example in his model of the helium atom with two electrons, and has treated the problem of valency from a new and convincing point of view, which we shall adopt in the next section. In the case of lithium, he adopted the configuration already discussed, not because his theory definitely required it, but because it seemed most likely to lead to the chemical properties of lithium. Since, however, lithium, if it has 3 electrons, must have only one ring, its valency, together with those of beryllium and boron, must be re-examined.

### *The Valencies of Elements.*

Bohr has given a partial analysis of this question, which, in so far as it relates to hydrogen and helium, is complete.

Let  $W_0$  be the energy which is emitted during the formation of a hydrogen atom. Then  $W$ , the corresponding energy for an atom containing a nucleus  $Ne$  and a ring of  $n$  electrons, is

$$W = nW_0 \left( N - \frac{1}{4} S_n \right)^2.$$

Bohr takes, as a criterion, that the formation of one system from another is possible if, and only if, the value of  $W$  is greater for the new system than for the old. Thus, if a system with  $n$  electrons can lose an electron,

$$f(n, N) < f(n-1, N),$$

and if it can gain one,

$$f(n, N) < f(n+1, N)$$

where 
$$f(n, N) = n \left( N - \frac{1}{4} S_n \right)^2.$$

We may consider the various systems with one ring in turn, identifying them with the elements of the Periodic Table.

(1) *Lithium*,  $N=3$ .

$$\begin{aligned} f(3, 3) &= 17.607, & f(4, 3) &= 16.694, & f(5, 3) &= 13.178, \\ f(2, 3) &= 15.13, & f(1, 3) &= 9. \end{aligned}$$

$f(3, 3)$  is the largest value, and therefore lithium should be an inert element like helium.

(2) *Beryllium*,  $N=4$ .

$$f(4, 4) = 37.037, \quad f(3, 4) = 35.142, \quad f(5, 4) = 34.414.$$

Beryllium should also be inert.

(3) *Boron*,  $N=5$ .

$$f(5, 5) = 65.65, \quad f(4, 5) = 65.38, \quad f(6, 5) = 60.39.$$

Boron might take up one electron, but could not retain it under ordinary circumstances.

(4) *Carbon*,  $N=6$ .

$$\begin{aligned} f(6, 6) &= 104.466, & f(5, 6) &= 106.885, \\ f(4, 6) &= 101.724, & f(7, 6) &= 95.578. \end{aligned}$$

Carbon should be monovalent and of a metallic nature.

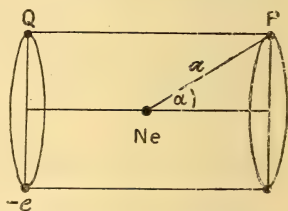
(5) *Nitrogen*,  $N=7$ .

$$\begin{aligned} f(7, 7) &= 154.315, & f(6, 7) &= 160.536, & f(5, 7) &= 158.120. \\ f(4, 7) &= 146.068, & f(8, 7) &= 140.784. \end{aligned}$$

and nitrogen should be divalent and metallic.

Thus the valencies are not in accord with experience, and if the electrons in the atoms are to be in one plane, we must either abandon this method of calculating valency,—and on any other method there would apparently be difficulty concerning the valency of helium,—or give up van den Broek's hypothesis, and suppose that the order in the Periodic Table does not correspond in a very simple manner with the atomic number, or charge of the central nucleus.

But the possibility of non-coplanar rings must be considered, and for this purpose we take an atom with nucleus  $4e$  and four electrons, arranged in two parallel rings, as in the figure. The rings are of equal radius, so that the condition of angular momentum is secured. The electrons are at any instant at the corners of a rectangle which can be inscribed to a circle. Let  $a$  be the radius of the circle and  $\alpha$  the angle shown in the figure.



If the electron P experiences no force along QP,

$$\frac{e^2}{a^2} \left( N - \frac{1}{4} \right) \cos \alpha = \frac{e^2}{4a^2} \sec^2 \alpha,$$

or

$$\cos^3 \alpha = \frac{1}{4N-1} = \frac{1}{15}$$

if the atom is electrically neutral.

For the steady rotation of the same electron,

$$m\omega^2 a \sin \alpha = \left( N - \frac{1}{4} \right) \frac{e^2}{a^2} \sin \alpha - \frac{e^2}{4a^2} \operatorname{cosec}^2 \alpha,$$

$$\text{or } \omega^2 = \frac{e^2}{ma^3} \left( N - \frac{1}{4} - \frac{1}{4} \operatorname{cosec}^3 \alpha \right) = \frac{e^2}{4ma^3} (15 - \operatorname{cosec}^3 \alpha)$$

where  $a$  is the radius of the atom.

We find  $\operatorname{cosec}^3 \alpha = 1.30923$ , and therefore

$$\omega^2 = (3.42269) \frac{e^2}{ma^3}$$

gives the angular velocity of the system in steady motion.

The angular momentum of each electron round the axis of the atom is

$$ma^2 \omega \sin^2 \alpha = h/2\pi$$

where  $h$  is Planck's constant, and the kinetic energy of the configuration is

$$W = 2ma^2 \omega^2$$

where  $W$  is also the energy required to remove the electrons to infinite distances from the nucleus and from each other. Eliminating  $a$  and  $\omega$  from these equations, we find

$$W = \frac{8\pi^2 m e^4}{h^2} \sin^4 \alpha (3 \cdot 4227)^2 \\ = 4W_0 \sin^4 \alpha (3 \cdot 4227)^2,$$

where  $W_0$  is the corresponding energy for a hydrogen atom. This leads on calculation to

$$W = 32 \cdot 732 W_0,$$

whereas, by a previous result, when the four electrons move in the same orbit,

$$W = 37 \cdot 037 W_0.$$

Although the value in the present case is smaller, we may suppose, as Bohr does in the case of his models for the lithium and beryllium atoms, that it corresponds to a possible neutral system. When one electron is removed, the remaining three must form one ring with, as already calculated,

$$W = f(3, 4) = 35 \cdot 142 W_0,$$

which is larger. Thus, such a system can lose an electron. Moreover, since

$$f(2, 4) = 2 \left( 4 - \frac{1}{4} \right)^2 = 28 \cdot 12,$$

we find that it cannot, in the same way, lose two electrons. The present atom is accordingly metallic, with a unit valency, and would be capable, from this point of view, of representing the lithium atom.

Although, accordingly, it is difficult to imagine what the chemical element with atomic number  $N=3$  can be, unless we postulate the existence of an unknown element between helium and lithium, with similar properties to helium, we see that with suitable modifications, Bohr's theory of the more complex atoms can apparently continue to represent the facts for at least some distance in its development, but in order to do so, it must abandon van den Broek's hypothesis. But, of course, outstanding difficulties remain. For example, if such a lithium atom ever lost an electron, it seems more probable that when the electron returned, the atom would take up the chemically inert configuration with a single ring. Even on Bohr's original lithium model, a chemically inert form must be regarded as the more usual one, if the method of estimating valency is to retain its meaning.



*X-ray Spectra.*

The considerations already given may evidently be applied in a general way to rings of electrons which are not coplanar, and we may conclude,—a conclusion supported by a further analysis not given in this paper,—that any such rings, preserving equality of angular momentum of all electrons, must as a rule be of the same radius.

Let us assume, in the preliminary consideration of Moseley's results, referred to in the introductory paragraph, that the X-ray spectra come from a ring of electrons not greatly disturbed by other rings, and treat this ring from the point of view of Bohr's theory, for Moseley, in applying this theory, has used an erroneous formula, to which the theory does not naturally lead.

If every electron in the ring has an angular momentum  $\tau h/2\pi$ , where  $\tau$  is a whole number, we have, in the usual notation, if  $\omega$  and  $a$  are the angular velocity and radius of the ring

$$\omega^2 = \frac{e^2}{ma^3} \left( N - \frac{1}{4} S_n \right), \quad ma^2 \omega = \tau h/2\pi.$$

The total kinetic energy of the electrons is

$$W = \frac{1}{2} mna^2 \omega^2,$$

and  $W$  is the energy which is radiated in the passage of the ring from a state of infinite dispersion into its present configuration. We find

$$W = \frac{2\pi^2 me^4}{h^2 \tau^2} n \left( N - \frac{1}{4} S_n \right)^2.$$

In passing between two stationary states, the frequency emitted is

$$\nu = \frac{2\pi^2 me^4}{h^3} \cdot n \left( N - \frac{1}{4} S_n \right)^2 \left( \frac{1}{\tau_1^2} - \frac{1}{\tau_2^2} \right),$$

where  $2\pi^2 me^4/h^3$  is the constant which agrees so closely with the universal constant of spectra.

The formula used by Moseley in his interpretation is, on the other hand,

$$\nu = \frac{2\pi^2 me^4}{h^3} \left( N - \frac{1}{4} S_n \right)^2 \left( \frac{1}{\tau_1^2} - \frac{1}{\tau_2^2} \right)$$

and omits the factor  $n$ . This has a vital effect on the conclusions which he has drawn. For he takes  $\tau_1 = 1$ ,  $\tau_2 = 2$  as

characterizing the principal vibration of the atom, thus obtaining, if  $\nu_0$  denotes  $2\pi^2 me^4/h^3$ ,

$$\nu = \frac{3}{4} \nu_0 \left( N - \frac{1}{4} S_n \right)^2,$$

and everything in his paper which appears to support the origin of the X-ray spectra from Bohr's theory depends on the factor  $\frac{3}{4}$ . The doubtful character of an argument based on the coincidence of the experimental constant with  $\frac{3}{4}$  has been emphasized by Dr. Lindemann\* in a recent discussion, for there is a large choice of values possible to  $\tau_1$  and  $\tau_2$ . But as we see, on Bohr's theory, that constant should not be  $\frac{3}{4}$ , but 3, if the ring contains four electrons. For Bohr's theory definitely stipulates that *in passage from one stationary state to another, only one quantum of energy is radiated from the atom*†. If four quanta, or one quantum for each electron in the ring, were evolved, the constant  $\frac{3}{4}$  would be obtained, but only with this modification of Bohr's hypothesis.

We shall examine the two alternatives separately. In the first place, let us adhere to Bohr's view, that one quantum only is concerned. Then

$$\nu = \nu_0 n \left( N - \frac{1}{4} S_n \right)^2 \left( \frac{1}{\tau_1^2} - \frac{1}{\tau_2^2} \right)$$

or, as expressed in wave-lengths, as tenth metres,

$$\lambda = \frac{3647 \cdot 14}{4} \cdot \frac{\tau_1^2 \tau_2^2}{\tau_2^2 - \tau_1^2} \cdot \frac{1}{n(N - \frac{1}{4} S_n)^2}.$$

With  $\tau_1 = 1$ ,  $\tau_2 = 2$ ,

$$\lambda = \frac{1 \cdot 21571}{n(N - \frac{1}{4} S_n)^2} 10^{-5} \text{ cm.}$$

should be the principal X-ray from a ring of  $n$  electrons surrounding a nucleus  $Ne$ . The principal X-ray of calcium has a wave-length

$$\lambda = 3 \cdot 368 \cdot 10^{-8} \text{ cm.,}$$

so that, for the ring producing it,

$$n(N - \frac{1}{4} S_n)^2 = (1215 \cdot 71) / (3 \cdot 368) = 360 \cdot 96,$$

or almost precisely 361. This is satisfied very accurately by  $N=19$ ,  $n=1$ , but  $N=20$ , the supposed atomic number of calcium, gives no good approximation at all, for any value of  $n$ , and the same applies to any number close to it except 19.

\* 'Nature,' Feb. 5, 1914.

† Phil. Mag. July 1913, p. 13.

A single inner electron cannot be regarded as likely on any theory.

Let us suppose, on the other hand, that there is only one ring in the atom, so that

$$N(N - \frac{1}{4}S_N)^2 = 360.96.$$

The nearest solution is  $N=10$ , which gives

$$10(10 - \frac{1}{4}S_{10})^2 = 376.63.$$

Thus the atom of calcium would only contain half the usual number of electrons assumed. By taking other values of  $\tau_1$  and  $\tau_2$ , we obtain very diverse results.

Suppose again, that a modification of Bohr's theory is taken, which makes the ring emit a number of quanta equal to the number of contained electrons, when passing from one state to another. Then we can obtain Moseley's solution  $N=20$ ,  $n=4$ . But it is only one of a whole set of solutions, none of which gives the other X-ray of calcium, obtained by attaching different values to  $\tau_1$  and  $\tau_2$ , and it is obtained on an assumption contrary to Bohr's own theory.

Moreover, from the considerations given earlier, it does not seem possible to arrange the other 16 electrons in the atom. The supposition of a neutral atom with one ring can in this case be shown to require 57 electrons, which is evidently an impossible number. In conclusion, we may say that even if the factor  $\frac{3}{4}$  were correct, Dr. Lindemann's objection would have considerable force, and, so far as they have been discussed at present, Moseley's observations have shown no relation to Bohr's theory,—though it cannot be argued from this fact that they possess none, or that the theory, in so far as it relates to spectra, is incorrect.

It appears to the writer that Moseley has really shown that the *frequencies of the principal X-rays of the elements are proportional to the squares of natural numbers*. This is a remarkable result which must lead to further knowledge of atomic structure.

It is evident that further confirmation or otherwise of Bohr's theory should be sought more directly in its application to the further elucidation of the spectra of the simple elements hydrogen and helium, for the whole ordinary spectrum of helium, and the secondary or vacuum tube spectrum of hydrogen remain to be interpreted. The writer hopes shortly to publish the results of a consideration of these questions.

LXV. *Induction-Coil Potentials.* By E. TAYLOR JONES, D.Sc., Professor of Physics in the University College of North Wales, Bangor\*.

[Plate VIII.]

THE present paper contains some further applications of the theory of electrical oscillations in coupled circuits, and is a continuation of two former papers † on the subject.

In the first of these it was shown that if a given current is interrupted in the primary of two coupled oscillatory circuits, the potential-difference,  $V_2$ , at the terminals of the secondary at any subsequent time  $t$  is theoretically given by an expression of the form

$$A_1 e^{-k_1 t} \sin(2\pi n_1 t - \delta_1) - A_2 e^{-k_2 t} \sin(2\pi n_2 t - \delta_2), \dots \quad (1)$$

where  $n_1, n_2$  are the frequencies of the two oscillations of the system, and the other six constants can be calculated from the capacities, inductances, and resistances of the circuits. This result was illustrated by a number of examples in which coupled air-core coils connected to condensers were used. The wave of potential represented by (1) was worked out for each case and compared with the experimental curve obtained with an electrostatic oscillograph.

In the second paper referred to, the expression (1) was further illustrated by experiments with an ordinary induction-coil with iron core, a number of cases being worked out in some of which the secondary coil, as well as the primary, was connected to a condenser. In these experiments, however, the primary (paraffin-paper) condenser was of considerably greater capacity than that generally used with an induction-coil.

Recently an expression of the form (1) has been given in an important paper by Dibbern ‡ for the potential-difference at the plates of the *primary* condenser, and the theoretical curves of both primary and secondary potential compared with the experimental curves obtained with a pendulum interruptor. In his experiments Dibbern used coils with air-cores, cores of iron-filings in paraffin-wax, of iron wire, and of solid iron. Good agreement was found between the

\* Communicated by the Author.

† "Electrical Oscillations in Coupled Circuits," E. T. Jones, *Phil. Mag.* xvii. p. 28 (1909); "The Induction-Coil," E. T. Jones and D. E. Roberts, *Phil. Mag.* xxii. p. 706 (1911). These two papers will be referred to as *l. c.* (1) and *l. c.* (2).

‡ E. Dibbern, *Ann. d. Physik*, xl. 4, p. 935 (1913); *Inaug.-Diss.*, Kiel.



theoretical and experimental curves for the coils with air-core and with the core of iron-filings, fair agreement in the case of the iron-wire core.

In the present paper further tests are described of the applicability of the theory to the case of an induction-coil. In these, smaller primary capacities were used, and the constants of the circuits were determined in actual working conditions. The effect of varying the primary capacity is specially considered, and a view is put forward which differs from that usually held as to the function and the most effective value of this capacity.

There are two things which should be borne in mind in determining the constants of the primary and secondary circuits of an induction-coil. The first is that, owing to the variable permeability of the core, it is necessary to use mean values of the induction-coefficients, which can only be expected to give correct values for the secondary potential over a limited range of values of the primary current.

The other is that the induction-coil as generally used has the terminals of its secondary coil connected to bodies of very small capacity, *e. g.* spark-gap terminals, the electrodes of an exhausted tube, or an electrometer or electrostatic oscillograph of very small capacity. In these circumstances, the capacity of the secondary circuit is mainly distributed along the secondary coil, and when the oscillations are taking place and no discharge is passing, the current is not uniform throughout the length of this coil, but is greatest at the central winding and very nearly zero at the terminals\*. The system is in fact similar to that of the oscillation transformer, or Tesla coil, the theory of which was given by Drude†.

The expression "mutual inductance" is not appropriate to such a system, but if (in Drude's notation)  $L_{12}$  is the coefficient of induction of the secondary on the primary, and  $L_{21}$  that of the primary on the secondary, then  $L_{12}$  is less than  $L_{21}$ .  $L_{12}$  is defined as the magnetic induction through the primary coil due to the secondary current divided by the value of the latter in the central winding. On the other hand, the terminals of the primary coil are connected to a condenser of considerable capacity, so that the current in this coil is uniformly distributed. The coefficient  $L_{21}$  is

\* As the current varies (in its fundamental oscillation) as the cosine of an angle proportional to the distance from the central winding, this distribution of current will be referred to as a cosine distribution.

† Drude, *Ann. d. Physik*, xiii. p. 512 (1904).

therefore equal to the "mutual inductance" of the coils as usually defined, *i. e.* the induction through the secondary due to the primary current divided by the value of the latter.

For similar reasons the self-inductance  $L_2$  of the secondary coil is less than the value for steady or for uniformly distributed currents, while  $L_1$  has the usual meaning. The coefficient of coupling,  $k$ , of the coils is defined by

$$k = \sqrt{L_{12} \cdot L_{21} / L_1 L_2}.$$

The value of the secondary capacity,  $C_2$ , depends upon the manner in which the charge is distributed in the secondary coil, but it is unnecessary to determine it. For the purpose of calculating the secondary potential  $V_2$  from the expression (1) it is sufficient to know the values of the six quantities  $L_1 C_1$ ,  $L_2 C_2$ ,  $L_{21}$ ,  $k$ ,  $R_1/L_1$ ,  $R_2/L_2$ .  $R_1$  and  $R_2$  are the effective resistances of the primary and secondary circuits.

These six quantities were determined as described below for an 18-inch-spark coil \*, with three primary condensers of capacities about 3, 2, and 1 microfarad respectively. These condensers had mica insulation, and for the sake of definiteness were connected directly across the terminals of the primary coil. If the condenser is connected across the interruptor in the usual manner, the primary circuit then includes the battery, amperemeter, and rheostat, and the self-inductance and resistance of the primary circuit will, therefore, be different in different experiments.

The secondary terminals were connected directly to the oscillograph, in parallel with which was a variable spark-gap consisting of two brass spheres, each 2 cm. in diameter, supported on ebonite pillars. The oscillograph has been described in a former paper †. The instrument has very small electrostatic capacity, and in its present form it can be used directly for potentials sufficient to give a 24-cm. spark between the ball electrodes.

#### *Determination of $L_{21}$ .*

This coefficient, which, as explained above, is equal to the mutual inductance of the primary and secondary coils, was determined by two methods. In the first it was compared with a known mutual inductance by the ballistic galvanometer

\* The primary coil was in four sections. Except where otherwise stated these were all in series.

† E. T. Jones, *Phil. Mag.* xiv. p. 238 (1907). *Cf.* also *l. c.* (2), p. 708.

deflexion method. The value so found was 20·4 henries for a primary current of 5 amperes. By comparison with this, the same method being used, values of  $L_{21}$  were then obtained for other values of the primary current  $i_0$ . The results are given in Table I.

TABLE I.

$i_0$ , amperes.	$L_{21}$ , henries.	$i_0$ , amperes.	$L_{21}$ , henries.
0·195	12·9	2·49	20·0
0·395	14·7	3·00	20·2
0·57	16·0	3·52	20·3
0·75	16·9	4·00	20·4
1·00	17·8	5·00	20·4
1·25	18·6	6·86	20·3
1·50	19·0	8·01	19·9
1·75	19·2	10·06	19·0
2·00	19·6	11·04	18·4

It will be seen from the table that  $L_{21}$  has its maximum value at 4 or 5 amperes, and that over the range 3 to 7 amperes it does not vary by more than 1 per cent. As most of the experiments described below were within this range, the value 20·4 was adopted for  $L_{21}$  in working out the theoretical expression (1) for the secondary potential.

The other method of determining  $L_{21}$  is to take the value of  $k^2$  measured with a condenser of considerable capacity in the secondary circuit, as described in the next section, in which case

$$k^2 = M^2/L_1L_2 = L_{21}^2/L_1L_2.$$

The values of  $L_1$ ,  $L_2$  being found from the periods of oscillation of the primary and secondary circuits when connected to condensers of known capacity,  $L_{21}$  can then be calculated from

$$L_{21} = \sqrt{k^2 L_1 L_2}.$$

The values found were

$$k^2 = \cdot 839, \quad L_1 = \cdot 194 \text{ henry}, \quad L_2 = 2540 \text{ henries.}$$

Hence

$$L_{21} = 20\cdot 3 \text{ henries,}$$

which is almost identical with the maximum value found by the other method. It may be concluded that up to the

frequencies used in this experiment the induction coefficients of the coils are not very different from their values for steady currents.

### *The Coefficient of Coupling.*

The coupling coefficient,  $k$ , was determined by finding the frequency of the oscillations of the secondary coil (connected only to the oscillograph and ball electrodes), with the primary coil open and with the primary terminals connected by a short piece of wire. The ratio of the squares of these frequencies is  $1 - k^2$ . These oscillations were started by sparking to the ball electrodes with two pointed conductors connected to a second induction-coil, and the curve of potential was photographed in the usual way. With the primary closed the oscillation curve only appeared with great difficulty, and many exposures were taken before a photograph sufficiently good for measurement was obtained. The amplitude of the curve was small, but was sufficient to allow the period to be determined with fair accuracy. The frequency was found to be 1246. With the primary open the frequency was 599.4. This was measured near the end of the curve where the amplitude, and consequently the magnetizing current, is small, in order to minimize as far as possible any error arising from the difference in the degree of magnetization of the core in the two experiments due to the shielding action of the induced current in the primary when on closed circuit.

These frequencies give the value .768 for  $k^2$ . The value given in the former paper\* for the same two coils was .8142. This was determined by a similar method, in which, however, a condenser was connected to the terminals of the secondary coil. It appears, therefore, that the coefficient of coupling of the coils (for natural oscillations) is less when the terminals of the secondary coil are free or connected to bodies of very small capacity, than when they are connected to a condenser of considerable capacity, in which case the oscillating current in the secondary is more nearly uniformly distributed.

The matter was further tested by determining the coupling coefficient with the secondary coil connected to various capacities, the largest being a leyden-jar of about .001 microfarad, and the smallest consisting of two tinfoil sheets, 19.94 square centimetres in area, separated by a glass plate

\* *L. c.* (2), p. 716.



0.61 cm. thick. The results are given in Table II., the capacities being in descending order of magnitude.

TABLE II.

Condenser.	Frequency with primary		$k^2$ .
	open.	closed.	
A .....	99.1	247.3	.839
B .....	218.0	519.0	.824
C .....	276.0	630	.808
D .....	355.6	792	.798
E .....	408.0	897	.793
F .....	455.0	989	.788
none .....	599.4	1246	.768

Specimens of the photographs used in these measurements are shown in Plate VIII. figs. 4 & 5. In fig. 4 the first three waves correspond to the exciting spark, the remainder to the free oscillation. The lower wave is the trace of a 768 tuning-fork photographed simultaneously. The numbers in the fourth column show a gradual falling off of the coefficient of coupling as the capacity connected to the secondary coil diminishes, *i. e.* as the current changes from the uniform to the cosine distribution. The question, however, arises whether this diminution of  $k^2$  is due to the change in the distribution of the current, or whether it is not due to some other cause, *e. g.* to a falling off in the intensity of magnetization of the core as the frequency of the oscillation increases. For a given potential at the terminals of the secondary condenser the magnetizing current diminishes as the capacity of the condenser diminishes, being in fact inversely proportional to the frequency of the oscillations. Hence it might be expected that the permeability of the core, for oscillations of given amplitude, would fall off as the capacity of the condenser diminishes. The question whether this appreciably affects the value of  $k^2$  was tested by repeating the experiment with the largest capacity (condenser A) with a much smaller potential. The method was the same, but a much smaller discharge was employed for starting the oscillation, and the most sensitive form of electrometer\* was used for obtaining the curve. The potential and current in this experiment were not more than one-fifth of those employed in the former determination, and the value of  $k^2$  obtained was .820. Hence the

\* Cf. Phil. Mag. xiv. p. 240 (1907).

diminution of the intensity of magnetization of the core with increasing frequency is not sufficient to account for the large falling off in the value of  $k^2$  shown in Table II.; and we may conclude that the drop in  $k^2$  is due to the change in the distribution of the current in the secondary coil, *i. e.* that as the current changes from the uniform to the cosine distribution, the coefficient  $L_{12}$  diminishes more rapidly than  $L_2$ . It would be interesting to make similar measurements of  $k^2$  for coils of different dimensions and forms, especially coils with non-magnetic cores.

In the above method for measuring  $k^2$  the oscillations were all started by sparking to the terminals of the secondary coil. There is, however, another way of setting up the oscillations with the primary coil closed, which may be referred to here. If the interruptor of an induction-coil is connected in a shunt across the primary coil, instead of being in the main circuit as usual, when contact is made the primary coil becomes short-circuited and its current begins to decay exponentially. At the same moment oscillations of small amplitude are set up in the secondary, and these are the natural oscillations of the secondary with the primary closed. The potential at the terminals of the secondary coil may be represented by the expression  $ae^{-kt} + b \sin nt$ , and the electrometer (being connected idiostatically) shows a deflexion which is proportional to the square of this quantity. This includes a term proportional to  $\sin nt$ , and another proportional to  $\cos 2nt$ . The curve should therefore show an oscillation of frequency  $n/2\pi$  and another of twice this frequency. As a rule the slower oscillation is much the more prominent, though traces of the octave appeared in some of the photographs.

The most prominent feature of the curves obtained was, therefore, an oscillation of frequency  $n/2\pi$ , *i. e.* the frequency of the oscillations of the secondary with primary closed, and not twice this frequency as is the case in the sparking method.

This "short-circuiting" method was tried with various capacities in the secondary circuit. Owing to the smallness of the amplitude of the oscillations, the most sensitive form of electrometer had to be used. The potential at the secondary terminals was in fact not sufficient to produce a 1 mm. spark between the ball electrodes.

The frequencies obtained by both methods are given for comparison in Table III., and one of the curves obtained by the short-circuiting method (no condenser) is shown in Plate VIII. fig. 6.

TABLE III.

Condenser.	Frequency of secondary.	
	Sparking method.	Short-circuiting method.
A .....	247.3	245.9
B .....	519.0	517.8
C .....	630	636
F .....	989	1026
none .....	1246	1266

It will be seen that there is no great difference between the results obtained by the two methods. Such differences as exist are to be accounted for by the difference in the circumstances of the experiments. In the sparking method the iron core is initially unmagnetized, and the oscillations are accompanied by reversals of the induced magnetism. In the short-circuiting method the core is initially strongly magnetized, and as the magnetization decays the oscillations produce small fluctuations in its intensity. The difference between the two cases may be illustrated by saying that, if  $N$  is the total flux of induction in the core and  $i$  the current in the secondary coil, then in the sparking method the frequency depends upon the coefficient  $N/i$ , whereas in the short-circuiting method it depends upon  $dN/di$ , and the value of this latter coefficient will be modified to some extent by the hysteresis of the core.

The circumstances of the sparking method are in closer accord with those of the actual case of an induction-coil, and the result obtained by that method, viz.  $k^2 = .768$ , is therefore adopted in the calculations of potential described below.

*Determination of  $L_1C_1$ ,  $L_2C_2$ ,  $R_1/L_1$ ,  $R_2/L_2$ .*

The expression (1) for the secondary potential was worked out for three cases in which mica condensers, of capacities stated to be 3, 2, and 1 microfarad respectively, were connected across the primary coil. These values were, however, not assumed, but rather the value of the product  $L_1C_1$  was determined for each case. This was done by coupling the primary (with the condenser across its terminals) loosely with a secondary of many windings to the terminals of which the electrometer was connected. The most sensitive electrometer

was used in order that the coupling of the two coils might be made as loose as possible. The oscillations were started by interrupting a current of 5 amperes in the primary, and the curves were photographed and measured in the usual way. The product  $L_1C_1$  was calculated from the frequency, the ratio  $R_1/L_1$  from the logarithmic decrement, of the oscillation curve. The results of these measurements are given in Table IV. The corresponding quantities for the secondary circuit,  $L_2C_2$  and  $R_2/L_2$ , were determined from the period and logarithmic decrement of the oscillation produced in the secondary when a current of 5 amperes in the primary was interrupted. In this experiment the primary condenser was removed, and the secondary coil was connected only to the electrometer and the ball electrodes, so that the secondary capacity was the same as in the final experiments. The values so determined are given under Table IV. It should be observed that these values of  $L_1C_1$  and  $L_2C_2$  are maximum values, *i. e.* they correspond to a magnetizing current of about 5 amperes in the primary coil.

The effective resistances of the coils in the circumstances of the present experiments, as determined from the damping of the oscillations, are much greater than their resistances for steady currents. The influence of these resistances on the periods of oscillation is, however, neglected in all calculations in the present paper, *i. e.* both in the determination of  $L_1C_1$  and  $L_2C_2$  described above, and in the calculation of the frequencies of the coupled system given in the next section. That no great error is thereby introduced is shown by the close agreement between the observed and calculated periods in the final experiments.

TABLE IV.

	$1/L_1C_1$ . C.G.S.	$R_1/L_1$ . C.G.S.
Case I. ....	$1.718 \cdot 10^6$	149
Case II. ....	$2.654 \cdot 10^6$	360
Case III. ....	$5.593 \cdot 10^6$	390
$1/L_2C_2 = 8.974 \cdot 10^6$ C.G.S., $R_2/L_2 = 215$ C.G.S.		



*Calculation of the Secondary Potential.*

The formulæ used in the calculation of the frequencies, amplitudes, and damping factors of the two oscillations are collected here :—

$$8\pi^2(n_1^2, n_2^2) = \frac{1}{1-k^2} \left[ \frac{1}{L_1 C_1} + \frac{1}{L_2 C_2} \right. \\ \left. \pm \sqrt{\left( \frac{1}{L_1 C_1} - \frac{1}{L_2 C_2} \right)^2 + 4k^2 \cdot \frac{1}{L_1 C_1} \cdot \frac{1}{L_2 C_2}} \right],$$

$$A_1 = \frac{2\pi L_{21} i_0 n_1 n_2^2}{(n_2^2 - n_1^2) \cos \delta_1},$$

$$A_2 = \frac{2\pi L_{21} i_0 n_1^2 n_2}{(n_2^2 - n_1^2) \cos \delta_2},$$

$$k_1 = 4\pi^2 n_1^2 \left( \frac{\theta_1 + \theta_2}{2} - \beta \right),$$

$$k_2 = 4\pi^2 n_2^2 \left( \frac{\theta_1 + \theta_2}{2} + \beta \right),$$

where

$$\theta_1 = \frac{1}{2} R_1 C_1 = \frac{1}{2} \frac{R_1}{L_1} \cdot L_1 C_1,$$

$$\theta_2 = \frac{1}{2} R_2 C_2 = \frac{1}{2} \frac{R_2}{L_2} \cdot L_2 C_2,$$

$$\beta = - \frac{2\pi^2 n_1^2 n_2^2}{n_2^2 - n_1^2} (\theta_1 - \theta_2) (L_1 C_1 - L_2 C_2),$$

and  $i_0$  is the current interrupted in the primary.

These expressions are, with a change of notation, the same as those used in the former papers.

In the case of the phase-angles  $\delta_1, \delta_2$ , however, new formulæ are required owing to the fact that in the former papers no account was taken of the difference between the effective resistances and the steady-current values. This affects the initial conditions of the problem, which now become at  $t = 0$ ,

$$-C_1 \frac{dV_1}{dt} = i_0, \quad V_1 = R_0 i_0^*, \quad \frac{dV_2}{dt} = 0, \quad V_2 = 0,$$

where  $R_0$  is the resistance of the primary for steady currents.

\* If the condenser is connected across the interruptor in the usual way the corresponding initial condition is  $V_1 = 0$ , and the solution for this case may be obtained by putting  $\theta_0 = 0$  in the final equation given below.

$V_1$  is the difference of potential at the terminals of the primary condenser which, for the reasons stated above, was connected directly across the primary coil.

The expression for  $V_2$  was accordingly worked out afresh for these new initial conditions, and the results show that the values of  $\delta_1$  and  $\delta_2$  are considerably modified by the change in the conditions. The expressions arrived at are

$$\tan \delta_1 = 2\pi n_1 \left\{ 2\beta \cdot \frac{n_1^2 + n_2^2}{n_2^2 - n_1^2} - (\theta_1 - 2\theta_0 - \theta_2) \right\},$$

$$\tan \delta_2 = \frac{n_2}{n_1} \cdot \tan \delta_1.$$

These reduce to the expressions used in the former papers if  $\theta_1$  is made equal to  $\theta_0$ , *i. e.*  $R_1$  to  $R_0$ .

In arriving at the above expressions the squares and product of  $\theta_1, \theta_2$  are neglected. The fuller expressions for  $\tan \delta_1$ ,  $\tan \delta_2$ , including these second order terms, were also, however, worked out for each of the three cases, and found to give values not differing greatly from those calculated from the above formulæ. The difference in  $\delta_1$  was in each case quite negligible, and in  $\delta_2$  less than  $1^\circ$  except in Case II., where it amounted to  $2^\circ.5$ . The values of  $\delta_1, \delta_2$  given in Table V. are those given by the more exact formulæ. This table contains the values of the eight constants of the formula (1) for each of the three cases, the amplitudes being given in volts for  $i_0 = 10$  amperes.

TABLE V.

	$n_1$ .	$n_2$ .	$A_1$ .	$A_2$ .	$k_1$ .	$k_2$ .	$\delta_1$ .	$\delta_2$ .
Case I. ....	194.3	1063	258000	49420	58	728	$-3^\circ.5$	$-17^\circ.7$
Case II. ....	232.8	1102	314600	75270	120	1130	$-7^\circ.1$	$-28^\circ.8$
Case III. ...	304.4	1224	416500	105400	96.5	1210	$-3^\circ.03$	$-11^\circ.4$

Values of the secondary potential were calculated from these by (1) for various values of  $t$ , squared (for comparison with the photographic curves), and plotted over one period of the slower oscillation. The curves are shown in figs. 1, 2, and 3, the maximum potentials indicated being in the three cases 238700, 291400, and 419000 volts respectively.

Fig. 1.

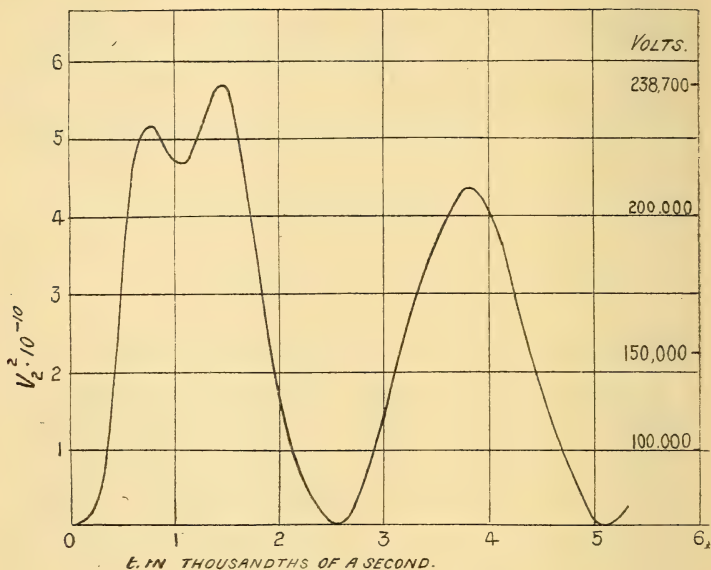
Case I.  $n_1=194.3$ ,  $n_2=1063$ .

Fig. 2.

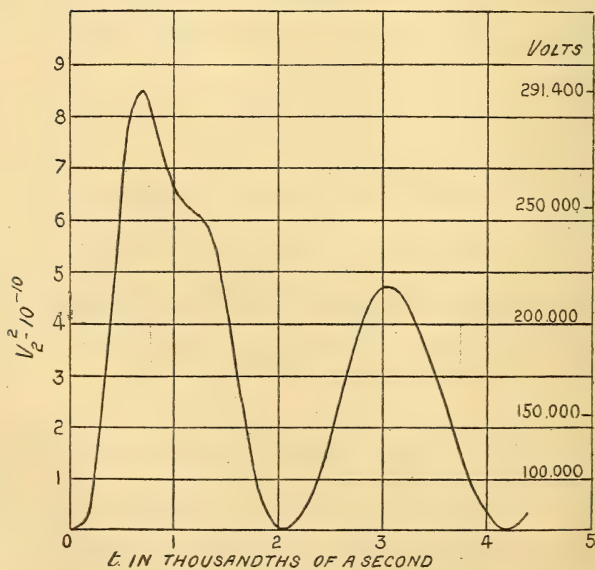
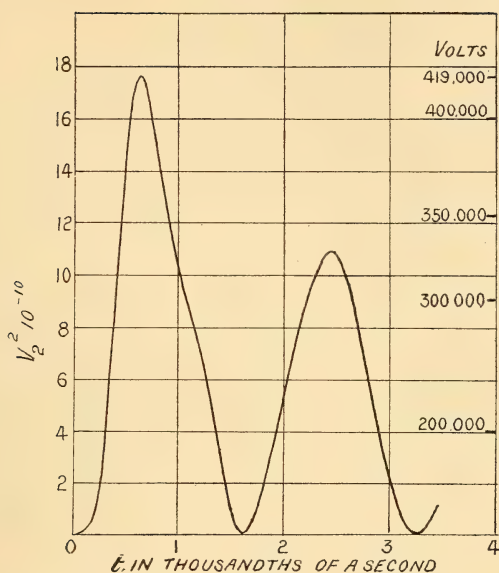
Case II.  $n_1=232.8$ ,  $n_2=1102$ .

Fig. 3.



Case III.  $n_1=304.4$ ,  $n_2=1224$ .

#### *Final Experiments and Conclusions.*

One of the experimental curves for each case is shown in Plate VIII. figs. 7, 8, 9 \*. In obtaining them the external circuit (*i. e.* the battery branch) was made as nearly non-inductive as possible, the connecting wires being well twisted together and the current being varied by changing the number of battery cells, rather than by inserting resistance coils. This was necessary because the primary condenser was connected directly across the coil. If a large battery and rheostat is used there is much sparking at the interruptor, and the maximum secondary potential is small and not even approximately proportional to the primary current. Two forms of interruptor were used, one consisting of a steel rod making contact with an iron plate, the other of an amalgamated copper rod dipping into mercury, in each case under paraffin oil. Even when the external circuit was nearly non-inductive there was generally sparking at the interruptor with the stronger currents, but occasionally a sparkless interruption occurred, accompanied by an exceptionally high potential in the secondary coil. The amplitude of the electrometer curve

\* The three photographs shown were obtained on different occasions, on which the electrometer had different degrees of sensitiveness.



was then unusually large, and these large amplitudes were alone selected for measurement. The iron-steel interruptor gave much more variable results than the other, but at its best was quite equal to the mercury interruptor.

A number of curves was first taken for different values of the primary current, in order to see whether the amplitude of the curve is proportional to the square of the current. Table VI. contains a set of results for Case I., the current being given in amperes and the amplitude  $A$  of the curve in millimetres.

TABLE VI.

$i_0$ .	$A$ .	$\sqrt{A}/i_0$ .
1.83	3.1	.962
2.81	7.8	.994
3.75	14.0	.998
4.91	23.3	.983
4.91	10.5	.660
6.41	16.9	.641

The last two plates were taken after the sensitiveness of the electrometer had been reduced by tightening the strip. In cases where the deflexion on the plate is over 3 cm. the photograph is generally very faint, and such large angular deflexions of the reflected ray probably cease to be proportional to the deflecting force.

The numbers in the third column of Table VI. show that over the range of this set of readings the maximum potential  $V_m$  at the electrometer is within 4 per cent. proportional to the current interrupted in the primary coil. Similar results were obtained, within the same limits, from the plates taken for Cases II. and III. The numbers given in the table also point to a maximum value of the ratio  $V_m/i_0$ , in the neighbourhood of 4 amperes, a result which might be expected from the manner in which  $L_{21}$  varies with  $i_0$ , as shown in Table I.

A set of three plates was next taken for the three cases with the same primary current, in order to see whether the maximum potentials are proportional to the calculated values. The results are given in Table VII. in which  $V_c$  represents the calculated value in volts of the maximum potential. In each case  $i_0$  was 3.0 amperes.

TABLE VII.

	A.	$V_c$ .	$V_c/\sqrt{A}$ .
Case I. ....	4.4	71610	34130
Case II. ....	6.9	87420	33310
Case III. ....	14.0	125700	33590

To within about 2.5 per cent., therefore, the calculated values of the maximum secondary potential are proportional to the values indicated by the electrometer.

With regard to the estimation of the absolute values of the potentials, no source of high potential suitable for standardizing the electrometer was available, and recourse was had to the method of spark potentials. It appears to be agreed that the potential difference required to produce a 1-centimetre spark, in air at atmospheric pressure, between ball electrodes 2 cm. in diameter, is not far from 31000 volts\*.

The above theoretical expression for  $V_2$  gives in Case I. a maximum value of 31000 volts at  $i_0 = 1.298$  amperes, but this is calculated on the assumption that the inductances are constant and equal to their maximum values. At this current, however,  $L_{21}$  is (from Table I.) about .916 of its maximum value, and we may assume that  $L_1$  and  $L_2$  are altered approximately in the same proportion. Hence from the expressions for  $n_1$ ,  $n_2$ ,  $A_1$ , and  $A_2$  we find that  $V_2$  is approximately proportional, as far as small variations in the permeability of the core are concerned, to the square root of  $L_2$ . Assuming this result, the calculated value of the current required to give a maximum voltage of 31000 is  $1.298/\sqrt{.916}$ , i. e. 1.356 amperes.

The least current observed to give a 1-cm. spark in Case I. was 1.36 amperes. This was repeated on many occasions and with both forms of interruptor, and found to be fairly definite. Sometimes the spark would not pass at less than 1.38 amperes, but on most occasions the result was as given above.

In Case II. the current giving 31000 volts, calculated

\* Feydweiller (Wied. *Ann.* xlviii. 1893) gives 31290 volts, while according to C. Müller (*Ann. d. Physik*, xxviii. 1909) the voltage is 30240. An account of the results of different observers is given in Fleming's 'Principles of Electric Wave Telegraphy and Telephony,' 2nd ed., pp. 26-8.

with correction for permeability, was 1.132 amperes. The observed least current giving a 1-cm. spark was 1.13 amperes, but generally a little more current was required. In Case III. the values were .815 ampere calculated, and .86 ampere observed. The difference is much greater in this case, but the correction for permeability is also greater and probably not so reliable.

Of the three cases Case I. gives the most definite value for the least sparking current, and is the most suitable to adopt as a standard, while the numbers in Table VII. show that the potentials in the other two cases are fairly closely proportional to the calculated values. The above results show therefore that, so far as the 1-cm. spark potential may be taken as a guide, the theoretical expression (1) leads to approximately correct values (within about 2.5 per cent.) of the maximum secondary potential over the range of current and primary capacity covered in the present experiments.

Further support of the theory is afforded by the similarity in the forms of the calculated and experimental curves (figs. 1, 2, 3, and Plate VIII. figs. 7, 8, 9), and by the agreement between the observed and calculated values of the frequency of the longer wave in each case. Thus the calculated frequencies are (from Table V.) 194.3, 232.8, 304.4 : the observed values, obtained by measurement of the photographs, 193.9, 232.3, 301.6.

Possibly still closer agreement between the calculated and observed results would have been found if second-order quantities (*e. g.*  $\theta_1^2$ ,  $\theta_2^2$ ) had been retained throughout but the additional labour involved in the calculations would make the method too cumbersome to be of much value. What is more required at present is a simplified expression which will give approximately the maximum secondary potential, or an upper limit to its value which is not very greatly in excess of the actual value.

Such an upper limit may be arrived at by neglecting the resistances of the circuits so that  $k_1$ ,  $k_2$ ,  $\delta_1$ , and  $\delta_2$  all become zero. If we further assume that the maxima of the two potential waves in the secondary occur simultaneously, the expression for the maximum potential becomes

$$2\pi L_{21}i_0 \frac{n_1 n_2^2 + n_1^2 n_2}{n_2^2 - n_1^2},$$

$$i. e. \quad 2\pi L_{21}i_0 \frac{n_1 n_2}{n_2 - n_1}.$$

This may also be expressed in terms of the ratio  $L_2 C_2 L_1 C_1$ .

Calling this  $m$ , and writing  $a$  for  $1/8\pi^2 L_2 C_2 (1-k^2)$ , we have

$$n_1^2 = a(m+1 - \sqrt{(m-1)^2 + 4k^2 m}),$$

$$n_2^2 = a(m+1 + \sqrt{(m-1)^2 + 4k^2 m}).$$

Thus

$$n_1^2 + n_2^2 = 2a(m+1),$$

$$n_1^2 n_2^2 = a^2 \{ (m+1)^2 - (m-1)^2 - 4k^2 m \},$$

$$= 4ma^2(1-k^2),$$

$$(n_2 - n_1)^2 = 2a(m+1) - 4a\sqrt{m(1-k^2)},$$

$$\frac{n_1^2 n_2^2}{(n_2 - n_1)^2} = \frac{2ma(1-k^2)}{m+1 - 2\sqrt{m(1-k^2)}},$$

and the upper limit to  $V_2$  is, for given  $L_{21}$ ,  $L_2 C_2$ , and  $v_0$ , proportional to the square root of this quantity.

If we wish to consider the effect of varying the primary capacity only, then the upper limit to  $V_2$  is proportional to the square root of

$$\frac{m}{m+1 - 2\sqrt{m(1-k^2)}},$$

or if

$$u = \frac{1}{m} = \frac{L_1 C_1}{L_2 C_2},$$

to the square root of

$$\frac{1}{1+u - 2\sqrt{u(1-k^2)}}.$$

This expression has a maximum value of  $1/k^2$  at  $u=1-k^2$ , and is equal to unity when  $u=0$ , *i. e.* when  $C_1=0$ . Consequently, if the resistances of the coils were negligible, the secondary potential might be expected to be greatest when the primary capacity  $C_1$  has a value of about  $L_2 C_2 (1-k^2)/L_1$ , and this maximum value would be about  $1/k$  times the value the potential would have if the primary condenser were removed altogether.

It is well known that for a given primary current there is a certain value of the primary capacity that gives a maximum secondary sparking distance with an ordinary interruptor\*, but it has been usual to attribute the inferiority of smaller capacities to their failure to prevent sparking at the interruptor, and the view appears to be generally accepted that with a sufficiently rapid interruption of the primary current

\* Cf. Walter, Wied. Ann. lxii. 1897; Mizuno, Phil. Mag. xlv. 1898.



the best effects would be obtained without any condenser. The above theory, however, points to a maximum spark-length with a certain condenser, at any rate in the case of negligible resistances, even with a perfectly sudden interruption.

The following experiments were therefore undertaken with a view to testing this point by observing the lengths of spark obtained with various capacities and different forms of interruptor. The condenser used was a subdivided mica microfarad, in which the fractions could be connected either in parallel or in cascade. This was in each case connected directly across the interruptor. The electrometer, though not used in these experiments, was left connected to the secondary coil in parallel with the ball electrodes, so that  $L_2C_2$  and  $h^2$  had the same values as in the experiments described above.

Experimenting first with the mercury interruptor and one secondary cell ( $i_0$  about 1.1 amperes), no amperemeter or rheostat being included in the circuit, it was found that the mica condenser was as a rule sufficient to prevent any visible spark at the interruptor, even when all its sections were in cascade. There was occasionally a spark at the interruptor but no account was taken of the result when this occurred. The capacities were taken in pairs, each two being tried alternately many times at the same distance. Thus .5 mfd. was found to give a longer spark than 1 mfd., .3 longer than .5. The longest spark was given by .05 mfd. Special attention was given to this capacity and .025 mfd., which were tried on many occasions. A distance could always be found at which .05 gave a spark every time, while .025 always failed. The distance was not the same on all occasions but was generally about 19.5 mm., and the difference of the sparking distances for these two capacities was about 1.5 mm. A longer spark was given by .05 than by .1 mfd., while .025 and .02 did not show any appreciable difference. A smaller capacity, in the form of an oil condenser of about .002 mfd., was tried, but in this case there was always sparking at the interruptor.

With the mercury break and one cell, therefore, the most effective capacity was about .05 mfd.\*, but there were indications of a second (smaller) maximum at about .3 mfd., this capacity giving consistently a rather longer spark than .2 mfd.

When tried with two cells, an amperemeter and a rheostat

\* The same result was found with a motor interruptor of the centrifugal type.

being connected in the primary circuit and the current kept at 2.0 amperes, similar results were obtained. At 103 mm. sparks passed freely with .05 mfd., none with .025. The smaller capacity also failed at 98 mm. At this current also .05 was superior to .1, and there was again a smaller maximum at about .3 mfd.

In the next experiments Lord Rayleigh's method of cutting the primary circuit with a projectile was followed, the object being to compare the two cases  $C_1 = .05$  mfd., and  $C_1 = 0$ . An air-gun was first used, which fires a pellet at about 500 feet per second. With one cell 19-mm. sparks were obtained every time with the condenser, none without the condenser at this distance or at 18 mm.

Still following Lord Rayleigh's plan \* a service rifle was next used. It was said to fire a bullet at 2000 feet per second. Again with one cell, at 19 mm. there was sparking every shot with the condenser, none with the condenser removed. With the condenser sparks also passed at 2 cm. Similar results were obtained with bullets reduced to about one-half, sparks passing at 19.6 mm. with the condenser, none without. At this distance .025 mfd. also failed.

With two cells ( $i_0$  about 2.2 amperes) the sparking distance was not so steady, and it was consequently more difficult to fix upon a distance which enabled one to decide in favour of the presence or absence of the condenser. The results were therefore not so conclusive, but whenever a difference was shown at consecutive shots it was always in favour of the condenser. Thus, of three successive shots with the balls at 125 mm., the first and third being without, the second with the condenser (.05 mfd.), the second alone gave a spark. The longest spark obtained without the condenser was 120 mm.

When an amperemeter and rheostat were connected in the primary circuit, and the current was kept at 2.0 amperes, the same condenser gave a spark at 111 mm., while at shots immediately before and after no spark appeared without the condenser. Again, at 107 mm. (reduced charge) no spark passed without the condenser, while at two shots with the condenser (before and after) a spark passed each time. In other instances two consecutive shots at the same distance showed a superiority of the condenser; in no such case did a spark pass without the condenser when it failed with the condenser †.

\* Phil. Mag. ii. p. 593 (1901).

† I am indebted to my colleague Mr. A. H. Ferguson, and to Mr. J. A. Owen, who joined me in the rifle experiments and verified the observations. I also wish to thank Sergt.-Major McCracken, of the College O.T.C., for his assistance in these experiments.

As far as these experiments go they do not support the view that the longest spark can be obtained without any primary condenser, but rather indicate a most effective capacity at about  $\cdot 05$  mfd.

The theory also points to this result. For, returning to the expression for the upper limit to  $V_2$ , which may be written  $L_{21}i_0U/\sqrt{L_2C_2}$ , where

$$U^2 = \frac{m}{m+1-2\sqrt{m(1-k^2)}},$$

and  $m = L_2C_2/L_1C_1$ , we find that in the present case  $U$  has a maximum at  $m = 4\cdot 31$ , *i. e.*  $C_1 = \cdot 144$  mfd., but that it does not vary by more than 3 per cent. over the range  $C_1 = \cdot 3$  to  $\cdot 05$  mfd.

Now the expression for  $U$  is arrived at on the supposition that the maxima of the two waves occur simultaneously, and these coincidences will take place (the resistances being neglected) when  $n_2/n_1 = 3, 7, 11, \dots$ . The values of  $n_2/n_1$  for various values of  $m$  can be calculated from the equation

$$\frac{n_2^2}{n_1^2} = \frac{m+1+\sqrt{(m-1)^2+4k^2m}}{m-1-\sqrt{(m-1)^2+4k^2m}}.$$

The least value of  $n_2/n_1$  occurs at  $m=1$  (*i. e.*  $L_1C_1=L_2C_2$ ), and is  $3\cdot 896$  at  $C_1 = \cdot 62$  mfd. The ratio  $n_2=3n_1$ , therefore, does not occur.

The next coincidence ( $n_2=7n_1$ ) occurs at  $m=9\cdot 798$ , giving  $C_1=\cdot 063$  mfd., and this is the coincidence which comes nearest to the maximum value of  $U$ . It is also within the range over which  $U$  is practically constant and equal to its greatest value. The longest spark should therefore be given by a primary capacity of about  $\cdot 06$  mfd. As described above the value actually found was  $\cdot 05$  mfd.

At  $n_2=5n_1$ , ( $C_1=\cdot 154$  mfd.) the maximum of the long wave occurs simultaneously with a minimum of the other, and a shorter spark is to be expected. At  $C_1=\cdot 3$  mfd. ( $n_2/n_1=4\cdot 194$ ) the maximum potential will be rather greater than at  $\cdot 154$  mfd. in consequence of the closer proximity of the maxima. These two cases were worked out by the expression (1), the damping factors  $k_1, k_2$ , and the phase angles  $\delta_1, \delta_2$  being neglected, with the result that  $\cdot 3$  mfd. gives a maximum potential about 5 per cent. higher than that given by  $\cdot 154$  mfd. A similar calculation shows that the maximum potential in the case  $L_1C_1=L_2C_2$ , *i. e.*  $C_1=\cdot 62$  mfd., is about 10 per cent. less than that given by  $\cdot 3$  mfd. The theory thus accounts for the observed

principal maximum spark-length at about  $C_1 = 0.5$  mfd., and for the second (smaller) maximum at about  $C_1 = 0.3$  mfd.

Other cases may be obtained by varying the self-inductance of the primary circuit. If, for example, the four sections of the primary coil are connected in parallel  $L_1$  is reduced to approximately one sixteenth,  $L_{21}$  and  $L_{12}$  to one quarter, of their former values, and  $k^2$  is unaltered. Calculating as above, we find that the maximum value of  $U$  is given by  $m = 4.31$ , *i. e.*  $C_1 = 2.304$  mfd. The nearest coincidence ( $n_2 = 7n_1$ ) occurs at  $m = 9.798$ , or  $C_1 = 1.013$  mfd., and the longest spark should be given by a capacity of about this value. By experiment the longest sparks were found to occur at  $C_1 = 1.025$  mfd., the variation being however very slight over the range 1.0 to 1.05 mfd.

A case of special interest is obtained by diminishing the coefficient of coupling so as to bring in the ratio  $n_2/n_1 = 3$ . The least possible value of  $n_2/n_1$  is  $\sqrt{(1+k)(1-k)}$ , consequently in order that  $n_2$  should be equal to  $3n_1$ ,  $k$  must not be greater than  $.8$ . In this case it is also possible to make the maximum value of  $U$ , and the ratio  $n_2/n_1 = 3$ , occur at the same value of the primary capacity. The necessary value of  $k^2$  is found by eliminating  $m$  between

$$m = \frac{1}{1-k^2}$$

and 
$$\frac{m+1+\sqrt{(m-1)^2+4k^2m}}{m-1-\sqrt{(m-1)^2+4k^2m}} = 9.$$

This leads to the equation

$$91k^4 - 164k^2 + 64 = 0$$

for  $k^2$ , giving  $k^2 = .571$ , the other root being greater than unity.

Consequently with  $k^2 = .571$  ( $k = .756$ ), and  $L_1 C_1 = .429$   $L_2 C_2$ , an exceptionally high secondary potential should be given by an induction-coil.

The most effective way of diminishing  $k^2$  is to introduce external self-inductance into the primary circuit, since this does not involve any diminution of  $L_{21}$ . In the present case (primary sections in series) the value of  $L_1$  required to give  $k^2 = .571$  is  $.241$  henry, and the primary capacity ( $C_1 = .429$   $L_2 C_2 / L_1$ ) is  $.198$  mfd. On trying the experiment it was found that by introducing the necessary external self-inductance the maximum spark-length for a given primary current was considerably increased. Thus at



$i_0=1.25$  amp. and without the external inductance the maximum spark-length ( $C_1=.05$  mfd.) was 2.81 cm.; with the external inductance and the same primary current the longest spark was 5.36 cm., and the most effective capacity for this case was .2 mfd.

The experimental results therefore agree with the theory in indicating that the most effective adjustment of the system (from the point of view of spark-length) is that in which  $n_2=3n_1$ , and  $U$  is at its maximum. It is probable that most induction-coils have coefficients of coupling which are greater than .8, and in such cases the method here described may be used for making the coil give a longer spark with a given primary current, or a given spark-length with a smaller current.

The actual values of the secondary potential can only be calculated when the effective resistances are determined for each case, but it is not probable that these latter results would be greatly modified by their introduction. On the whole the evidence tends to show that the theory described in this and the two former papers is sufficient for the calculation of the secondary potential of an induction-coil and the most effective value of the primary capacity.

Bangor, February 1914.

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LXVI. *The Diffusion and Valency of the Radio-elements.*

By G. HEVESY, Ph.D., Hon. Research Fellow in Physics, Manchester University\*.

IN 1912 the author undertook the direct determination of the valency of the radio-elements by the measurement of the velocity with which their ions diffuse in dilute acid solution†. Since the diffusion velocity of the ions depends only on their mobility and on their valency, and since the first of these quantities can only vary between narrow limits, the magnitude of the diffusion constant of the respective ions furnishes a direct measure of their valency, *i. e.* the number of charges which they carry.

Since that time the chemistry of the radio-elements has been examined in detail in a number of excellent researches‡,

\* Communicated by Sir E. Rutherford, F.R.S.

† Hevesy, *Phil. Mag.* [6] xxv. p. 390 (1913); *Phys. Zeit.* xiv. p. 50 (1913).

‡ Fleck, *Journ. Chem. Soc.* ciii. pp. 394 & 1052 (1913); Fajans and Beer, *Die Naturwissenschaften*, i. p. 388 (1913); W. Metzner, *Ber. d. Deutsch. Chem. Ges.* xlv. p. 979 (1913); Russell, *Chem. News*, cvii. p. 49 (1913); Fajans, *Phys. Zeit.* xiv. p. 131 (1913); *Ber. d. Deutsch. Chem. Ges.* xlv. p. 422 (1913); Soddy, *Chem. News*, cvii. p. 97 (1913).

some of an experimental and some of a theoretical nature; and from a consideration of the results obtained, it appeared necessary that a new and careful determination should be made of the diffusion constants of thorium B and radium E, for which the above method furnished a value of the valency too small by one unit. The possibility of such a result has already been discussed in the former papers\*.

The following paper contains also an account of the determination of the valency of actinium, and of the measurement of the degree of dissociation of lead chloride from diffusion data, and of some experiments on the diffusion of radio-elements in a colloidal state, together with a discussion on the possibility of separating chemically identical elements by means of diffusion.

*The Diffusion of the Chloride of Lead and the Chloride of Thorium B.*

To explain the behaviour of thorium B, the diffusion constants of lead chloride, of thorium B, and of thorium B mixed with lead chloride were measured, since it is supposed that thorium B and lead are chemically non-separable elements. The apparatus was identical with that described in former papers†. The determination of the diffusion velocity of lead chloride was made by finding the lead chloride content of thin layers which were evaporated to dryness after the interruption of the experiment, while that of thorium B was made by the comparison of the activities of similar layers. In the case of the simultaneous diffusion of thorium B and lead, such a small part of the solution was evaporated that the  $\alpha$  rays suffered no measurable absorption in passing the layer of lead chloride. The results obtained are given below.  $D$  is the diffusion constant expressed in sq. cm. per day, 0.57 is the constant of the apparatus, the first factor in the denominator gives the time of diffusion in days and the second is taken from Stephan's tables; it is a number which is a function of the ratio of the concentrations of the final and initial layers, and has come to be suitably referred to as "Stephan's number."  $I$ . is the diffusion constant calculated from the uppermost layer,  $II$ . that calculated from the second layer, and so on. The third layer, as is well known, is not suitable for the calculation of the diffusion constant‡.

\* Hevesy, *loc. cit.*

† Hevesy, *loc. cit.*

‡ Sv. Arrhenius, *Zeit. phys. Chem.* x. p. 53 (1892); W. Kanalkiv, *Wied. Ann.* lii. p. 183 (1894).

Diffusion into water of  $\text{PbCl}_2$  from a nearly saturated solution — 1/31 normal.

( $D_{16^\circ.2}$ ) is the diffusion coefficient measured at  $16^\circ.2$  C.

( $D_{18^\circ}$ ) is the diffusion coefficient calculated at  $18^\circ$  C., allowing 2.7 per cent. per degree for the temperature coefficient. This correction is deduced from the mobility of the ions.

		$D_{16^\circ.2}$ .	$D_{18^\circ}$ .
I.	$\frac{0.57}{2.02 \times 0.278}$ .....	1.03	1.08
II.	$\frac{0.57}{2.03 \times 0.278}$ .....	1.03	1.08
IV.	$\frac{0.57}{2.04 \times 0.293}$ .....	0.95	1.00
<hr/>			
I.	$\frac{0.57}{1.81 \times 0.316}$ .....	0.99	1.07
II.	$\frac{0.57}{1.83 \times 0.310}$ .....	1.03	1.11
IV.	$\frac{0.57}{1.85 \times 0.328}$ .....	0.94	1.02

Mean value  $D_{18^\circ} = 1.08$  sq. cm. per day.

From the equation  $D = \frac{0.0224}{n} U$ , where  $U$  is the mobility of the lead ions (or more correctly the resultant of the mobilities of the lead and chlorine ions, since the diffusion in this case does not take place in excess of anion, and so the chlorine ion somewhat increases the mobility of the lead ion) the valency is calculated to be 1.64.

This apparently strange result follows from the considerations given above, namely, that the diffusion is governed by the mobility and the number of charges on the ion. According to the work of v. Ende\*, such a result is to be expected, since in a saturated lead chloride solution there are present 6.2 per cent. lead molecules undissociated, 47.3 per cent.  $\text{PbCl}^\bullet$  ions and 50.1 per cent.  $\text{Pb}^{++}$  ions. About one half of the lead present will therefore possess one and the other half will possess two charges, and hence the lead molecules will diffuse as if they had 1.5 charges.

Calculating on the assumption that  $\text{PbCl}^\bullet$  ions have a velocity similar to that of  $\text{Pb}^{++}$  ions, one obtains from the diffusion constant of lead chloride a value for the degree of

\* v. Ende, *Zeit. Anorg. Chem.* xxvi. p. 162 (1903); Harkins, *J. Amer. Chem. Soc.* xxxiii. p. 1859 (1911).

dissociation similar to that obtained by v. Ende from a consideration of the influence of the addition of salt on the solubility of lead chloride.

For the diffusion constant of thorium B mixed with lead chloride the following values were obtained:—

			$D_{16^{\circ}2.}$	$D_{18^{\circ}.$
I.	$\frac{0.57}{2.02 \times 0.267}$	.....	1.05	1.10
II.	$\frac{0.57}{2.03 \times 0.280}$	.....	1.02	1.07
IV.	$\frac{0.57}{2.04 \times 0.279}$	.....	1.01	1.06
<hr/>				
I.	$\frac{0.57}{1.81 \times 0.316}$	.....	1.00	1.08
II.	$\frac{0.57}{1.83 \times 0.324}$	.....	0.98	1.05
IV.	$\frac{0.57}{1.85 \times 0.303}$	.....	1.01	1.09

Mean value for  $D_{18^{\circ}}$  is 1.07 sq. cm. per day.

In this experiment thorium B chloride ( $\text{Th B Cl}_2$ ) and lead chloride were mixed, and had therefore the same degree of dissociation, and they showed, within the limits of experimental error, the same coefficient of diffusion. Further, the velocity with which a 1/5000 N lead chloride and 1/100 N hydrochloric acid solution containing thorium B diffused into a 1/10,000 N hydrochloric acid solution was determined. The quantity of lead here was so small that a gravimetric estimation could not be carried out, and the diffusion constant was only ascertained by comparing the activities of single layers; the results were

			$D_{16^{\circ}2.}$	$D_{18^{\circ}.$
I.	$\frac{0.57}{1.93 \times 0.450}$	.....	0.67	0.70
II.	$\frac{0.57}{1.94 \times 0.457}$	.....	0.64	0.67
IV.	$\frac{0.57}{1.95 \times 0.463}$	.....	0.63	0.66

Mean value for  $D_{18^{\circ}}$  is 0.68 sq. cm. per day.

At this concentration, therefore, thorium B measured in lead chloride is almost completely dissociated, and possesses a diffusion constant characteristic of doubly charged ions.



An experiment, carried out under exactly similar conditions as the last but with the complete absence of lead chloride, gave an identical value for the diffusion constant as follows :—

		$D_{18^\circ}$ .	$D_{18^\circ}$ .
I.	$\frac{0.57}{2.20 \times 0.386}$ .....	0.67	0.70
II.	$\frac{0.57}{2.22 \times 0.393}$ .....	0.66	0.69
IV.	$\frac{0.57}{2.24 \times 0.408}$ .....	0.63	0.66

Mean value for  $D_{18^\circ}$  is 0.68 sq. cm. per day.

The diffusion constant of completely dissociated (thorium B) chloride gives, therefore, the value 2 for its valency, in complete agreement with Fleck's result\* from the chemical evidence that thorium B is non-separable from lead. The former value of 1 found by the author is not that of thorium B ions, but that of the complex (Th B)  $\text{Cl}_2$  ions which were predominant in a partially dissociated solution of thorium B.

#### *The Diffusion of Radium E.*

In order to avoid convection currents it is necessary that the specific gravity of the liquid in successive layers should vary somewhat. Even in the last experiment disturbances due to these currents were met with to some extent, but in the case of radium E these difficulties are multiplied. In order to obtain complete dissociation, diffusion must take place in dilute acid solution. To obtain a difference in the specific gravities of the two layers—the one containing radium E and the other free from that substance—an addition of 5 per cent. of ethyl alcohol was made to the latter. This addition did not influence the degree of dissociation† of radium E, but decreased its mobility slightly, and thus also its velocity of diffusion. In order to deduce the value of the diffusion velocity from the value thus obtained, one can either add a correction of 13 per cent. which follows from the determination of Arrhenius‡, or one can determine the diffusion velocity of radium D—the value of which for water has been determined in the same alcoholic solution as the radium E. This latter proceeding permits the elimination of any other effects of the addition of the alcohol. The diffusion constants which were obtained by

\* Fleck, *loc. cit.*; F. Paneth and G. Hevesy, *Wiener Ber.* p. 122 (1913).

† Sv. Arrhenius, *Zeit. phys. Chem.* x. p. 51 (1892).

‡ Arrhenius, *loc. cit.*

the diffusion of a radium E and radium D solution from a 1/1000 normal hydrochloric acid solution into one of the same strength, which was also 1 N with respect to alcohol, are given below. The experiment was carried out by measuring the activity of the layers immediately after interrupting a diffusion. This, with a very small correction for the disintegration of radium E during the time of the experiment, gave the diffusion constant of radium E. The ratios of the activities were then measured about a month later, after the radium D and radium E had attained equilibrium, and thus the diffusion constant of radium D was obtained.

## Diffusion constant of radium E.

		$D_{15^{\circ}2.}$	$D_{18^{\circ}.$
I.	$\frac{0.57}{1.75 \times 0.920}$ .....	0.36	0.39
II.	$\frac{0.57}{1.77 \times 0.945}$ .....	0.34	0.37
IV.	$\frac{0.57}{1.79 \times 0.905}$ .....	0.36	0.39

Average value for  $D_{18^{\circ}}$  is 0.38 sq. cm. per day.

## Diffusion constant of radium D.

		$D_{15^{\circ}2.}$	$D_{18^{\circ}.$
I.	$\frac{0.57}{1.75 \times 0.612}$ .....	0.53	0.57
II.	$\frac{0.57}{1.77 \times 0.623}$ .....	0.52	0.56
IV.	$\frac{0.57}{1.79 \times 0.615}$ .....	0.51	0.55

Mean value for  $D_{18^{\circ}}$  is 0.56 sq. cm. per day.

The addition of 5 per cent. of alcohol, therefore, lowered the diffusion velocity of radium D about 16 per cent. If the decrease is the same in the case of radium E, then the result is the value 0.45 for the diffusion constant of radium in water. This value is characteristic of an ion carrying three charges.

*The Diffusion of Actinium.*

An almost invisible quantity of an actinium-lanthanum preparation was dissolved in 1/100 N hydrochloric acid and allowed to diffuse into 1/1000 N hydrochloric acid. After the experiment had been going three days it was interrupted, the layers evaporated, and their  $\alpha$ -activities measured. This activity comes from the radio-actinium, actinium X, actinium emanation, actinium A, and actinium C which are present,

since it is well known that actinium itself emits no  $\alpha$ -rays. The diffusion constant, which is obtained by a comparison of the activities of the layers immediately after the interruption of the experiment, is not that of actinium but that of actinium X, or, to speak more correctly, the resultant of the diffusion constants of actinium X and radioactinium. The former predominates since the short lived products are present in equilibrium with actinium X.

Diffusion velocities measured by comparison of the activities immediately after the interruption of the experiment :—

			$D_{15^{\circ}}$ .	$D_{18^{\circ}}$ .
I.	$\frac{0.57}{0.307 \times 3.10}$	.....	0.60	0.65
II.	$\frac{0.57}{0.280 \times 3.12}$	.....	0.65	0.70
<hr/>				
I.	$\frac{0.57}{0.308 \times 3.0}$	.....	0.62	0.67
II.	$\frac{0.57}{0.275 \times 3.02}$	.....	0.68	0.73

Mean value for  $D_{18^{\circ}}$  is 0.69 sq. cm. per day.

This gives a valency of 2, which corresponds to that of actinium X.

The above measurements were made between the 9th and 13th November 1912, immediately after stopping the diffusion experiment, and the valency obtained is that corresponding to actinium X. The activities of the layers were taken about 200 days later, on the 5th of June 1913, after the radioactinium, actinium X, and the short lived products had come into equilibrium with actinium. The numbers obtained at that later date are as follows :—

Measured by comparison of the activities of the layers  
six months later.

			$D_{15^{\circ}}$ .	$D_{18^{\circ}}$ .
I.	$\frac{0.57}{0.444 \times 3.10}$	.....	0.41	0.44
II.	$\frac{0.57}{0.429 \times 3.12}$	.....	0.43	0.46
<hr/>				
I.	$\frac{0.57}{0.452 \times 3.00}$	.....	0.42	0.45
II.	$\frac{0.57}{0.424 \times 3.02}$	.....	0.44	0.47

Mean value for  $D_{18^{\circ}}$  is 0.46 sq. cm. per day, corresponding to the valency 3.

The valency of actinium is therefore 3, and this gives more evidence in favour of the view that actinium is the absent homologue of lanthanum. This determination is further of interest as there is no known element that should be non-separable from actinium, and therefore the methods which Fleck and others have used for the examination of the chemical nature of the radio-elements here fail.

In addition to the radio-elements the valency of which the author has determined from diffusion data, there are still mesothorium 1 and radiothorium, and also perhaps actinium B and radium  $C_1$ , to which the diffusion method might be applied. The diffusion velocities of three elements non-separable from mesothorium 1, and of four non-separable from radiothorium, have, however, been determined, so that these investigations offer little interest. The determination of the diffusion constants of a member of the thallium type, as for example that of radium  $C_2$ , thorium D, or actinium D, would, however, be of importance. Likewise of great interest would be the measurement of the velocity of diffusion of uranium  $X_2^*$ , which is a new type of element. It is unfortunate that the half-value period of the latter element is only of the order of one minute, and thus is far too short for measurements of its diffusion constant. In the case of all the other elements, it can be shown by the measurement of the velocities of diffusion of the respective ions that the change of valency that an atom experiences by disintegration is determined by the number and sign of the charges which that atom gives out in its transformation.

The diffusion constants and the corresponding valencies are given in the Table. It is not always that a perfect dissociation becomes manifest, for example, not in the case of uranium X, but nevertheless the valency can be determined with certainty in every case from the diffusion constant.

Since radium F and also radium A send double charged ions into solution, it cannot be determined from diffusion experiments alone whether the transition from the emanation takes place into the second or eighth group of the periodic system. I have previously put forward the suggestion that the former takes place, but this view has been shown to be erroneous.

\* Fajans & Gohring, *Die Naturwissenschaften*, i. p. 399 (1913); *Phys. Zeit.* xiv. p. 877 (1913). Hahn & Meitner, *Phys. Zeit.* xiv. p. 758 (1913); Fleck, *Phil. Mag.* xxvi. p. 528 (1913).



The number of charges on the radio-ions, calculated from their diffusion constants.	Diffusion constant in sq. cm. per day.
Uranium $X_1^{++++}$ .....	0.4
Ionium $^{++++}$ .....	0.33
Radium $^{++}$ .....	0.67
Radium $F^{++}$ (radium $A^{++}$ ) .....	0.76
Radium $D^{++}$ (radium $B^{++}$ ) .....	0.65
Radium $E^{+++}$ (radium $C_1^{+++}$ ) .....	0.45
Thorium $^{++++}$ .....	0.33
Thorium $X^{++}$ (mesothorium $I^{++}$ ) .....	0.66
Actinium $^{+++}$ (mesothorium $II^{+++}$ ) .....	0.46
Radiothorium $^{++++}$ .....	0.33
Thorium $X$ .....	0.66
Radium $F^{++}$ (thorium $A^{++}$ ) .....	0.76
Thorium $B^{++}$ .....	0.67
Thorium $C^{+++}$ .....	0.5
Actinium $^{+++}$ .....	0.46
Radiothorium $^{++++}$ (radioactinium $^{++++}$ ) ..	0.33
Actinium $X^{++}$ .....	0.66

*The Diffusion of Colloidal Radio-elements.*

(In collaboration with F. PANETH, Ph.D.)

Recently the question of diffusion has been approached from a different standpoint, namely, that under certain conditions the radio-elements are present in solution in a colloidal state. Paneth\* sought to separate radium D, E, and F from lead by means of dialysis, and found that radium D, just like lead, can pass through a membrane, but that in the cases of radium E and especially radium F only the smallest quantities could pass through. Paneth's† experiment points to the fact that radium E and F are present in a lead nitrate solution in a colloidal form.

\* F. Paneth, *Wiener Ber.* cxxi. p. 2193 (1912).

† F. Paneth, *Kolloid. Zeit.* xii. p. 1 (1913).

Godlewski\*, on the other hand, investigating the properties of solutions of the active deposit of radium in water, found that the charge of the particles can be changed by the addition of multi-charged cations and anions, a property which is highly characteristic of colloids. In order to obtain a further proof of the colloidal nature of such solutions and to obtain, by experiment, an estimation of the size of these small particles, the diffusion of radium D, E, and F and of thorium B in alkaline, neutral, and dilute acid solution was measured.

*Diffusion in Alkaline Solution.*

Alkaline solutions of the above-mentioned elements are not completely stable, since the particles discharge themselves as time goes on and are precipitated on the walls of the vessel. It is no longer sufficient, as in the diffusion of stable solutions, to determine the ratios of the concentrations of the initial and final layers of the diffusing substances, since the initial layer loses a part of its content through coagulation which will play no part at all in the diffusion†. After the termination of the experiment the concentrations of all the layers are determined and added together. The total value so obtained is taken as the content of the initial layer before the experiment began. The possible error that may be made by this assumption has the result that the velocity of diffusion seems somewhat greater than it actually is, and the substance therefore seems less colloidal; the actual value, however, is not substantially altered.

Diffusion of polonium into  $\frac{1}{2}$  N ammonia.

		$D_{16^{\circ}3.}$	$D_{18^{\circ}0.}$
I.	$\frac{0.57}{2.9 \times 0.85} \dots\dots$	0.23	0.24
II.	$\frac{0.57}{2.9 \times 1.5} \dots\dots$	0.13	0.14
III.	$\frac{0.57}{2.9 \times 0.92} \dots\dots$	0.21	0.22
IV.	$\frac{0.57}{2.9 \times 1.2} \dots\dots$	0.16	0.17

Mean value for  $D_{18^{\circ}0}$  is 0.19 sq. cm. per day.

\* Godlewski, *Bull. de l'Acad. d. Science de Cracovie* (1913).

† Frl. Meitner has already noticed the precipitation of radium C from solution by addition of ammonia; it is of interest to mention that the failure of the v. Lerch method in alkaline solution is due to radium C being present in a colloidal state.

## Diffusion of thorium B into 1/12 N ammonia.

			$D_{15^{\circ}8.}$	$D_{18^{\circ}0.}$
I.	$\frac{0.57}{1.8 \times 1.2}$	.....	0.37	0.39
II.	$\frac{0.57}{1.8 \times 1.3}$	.....	0.37	0.36
IV.	$\frac{0.57}{1.8 \times 1.3}$	.....	0.34	0.36

Mean value for  $D_{18^{\circ}}$  is 0.37 sq. cm. per day.

## Diffusion of thorium B into 1/14 N ammonia.

			$D_{15^{\circ}6.}$	$D_{18^{\circ}0.}$
I.	$\frac{0.57}{1.77 \times 0.83}$	.....	0.39	0.41
II.	$\frac{0.57}{1.77 \times 1.0}$	.....	0.32	0.34

Mean value for  $D_{18^{\circ}}$  is 0.37 sq. cm. per day.

Radium F, thorium B, and (as shown by a qualitative experiment), radium E also thus diffuse substantially more slowly in alkaline than in acid solution. They are therefore, in a great degree, present in alkaline solution in a colloidal form.

The diffusion constants found above are considerably smaller than those obtained for colloidal albumen and similar substances. However, it is not to be expected that in such extreme dilution as that of the material present in these solutions of radio-elements large particles would be formed. Moreover, similar diffusion constants were obtained in the case of colloidal gold solutions by Whitney and Blake \* as well as by Svedberg †. An attempt to estimate the size of these colloidal particles of radium F and thorium B can be made by using the equation  $D^2M=60$ . Substituting the different values of  $D$  in the various cases, one obtains in the first case an average value for the molecular weight of 1600 corresponding to an aggregate of 8 atoms, and in the second case a value of 460 corresponding to an aggregate of only two atoms.

*Diffusion in Neutral and dilutely Acid Solutions.*

Traube-Menganini and Scala have demonstrated the direct formation of colloidal metallic solutions by the bringing together of such metals as nickel, tin, etc., and distilled water, and then this colloidal metal is transformed under

\* Whitney & Blake, *J. Amer. Chem. Soc.* xxvi. p. 1363 (1904).

† Svedberg, *Zeit. phys. Chem.* lxxiv.

the action of secondary forces into colloidal hydroxides, &c. From the variety of such secondary forces one would expect a corresponding variety of results from diffusion experiments in those kinds of solutions. Thus the diffusion constant, measured in neutral solution, of thorium B which is similar to lead shows the electrolytic nature of the former, while polonium is still, to a large extent, colloidal in 1/1000 N hydrochloric acid solution.

Diffusion of thorium B from dilute KCl solution into water.

		$D_{15^{\circ}6.}$	$D_{18^{\circ}.$
I.	$\frac{0.57}{1.70 \times 0.46}$ .....	0.73	0.78
II.	$\frac{0.57}{1.70 \times 0.44}$ .....	0.76	0.81
IV.	$\frac{0.57}{0.46}$ .....	0.73	0.78

Mean value for  $D_{18^{\circ}}$  is 0.79 sq. cm. per day, which corresponds to 80 per cent. completely dissociated lead chloride.

Diffusion of thorium B from distilled water into 2 N alcohol.

		$D_{15^{\circ}2.}$	$D_{18^{\circ}.$
I.	$\frac{0.57}{1.81 \times 0.65}$ .....	0.48	0.52
II.	$\frac{0.57}{1.81 \times 0.56}$ .....	0.56	0.60
IV.	$\frac{0.57}{1.81 \times 0.67}$ .....	0.47	0.51

The value found for  $D_{18^{\circ}}$  must be multiplied by 1.13 \* to eliminate the retarding influence of the added alcohol, and the value for  $D_{18^{\circ}}$  thus becomes 0.61 sq. cm. per day. This is the diffusion constant of completely dissociated (ThB)Cl<sub>2</sub>.

Diffusion of radium F from 1/000 N hydrochloric acid solution into a hydrochloric acid solution of the same concentration which is also 1 N with respect to alcohol.

		$D_{15^{\circ}2.}$	$D_{18^{\circ}.$
I.	$\frac{0.57}{1.73 \times 0.90}$ .....	0.36	0.38
II.	$\frac{0.57}{1.75 \times 1.43}$ .....	0.23	0.24
III.	$\frac{0.57}{1.79 \times 1.45}$ .....	0.22	0.23
IV.	$\frac{0.57}{1.79 \times 1.45}$ .....	0.22	0.23

\* Arrhenius, *Zeit. phys. Chem.* x. p. 51 (1892).



This value must as usual be increased by 13 per cent. to eliminate the retarding influence of the alcohol.

Sometimes it is difficult to distinguish from diffusion data alone whether colloidal particles or ions with multiple charges are present; in both cases diffusion takes place slowly, in the first case because an aggregate of molecules which acts as a single molecule diffuses but with greater friction, and in the latter case, on account of the increased hydration of the ions which has the result of increasing the friction.

Colloidal particles are often considered as large ions\*. If the same considerations that have been used above to determine the number of charges on an ion are applied to find the number of charges on a colloidal particle, then the great number of charges is proved by the smallness of the diffusion velocity and by the proportionate great mobility of colloids in an electric field. If the colloidal particles had only one charge they would probably move in an electric field with a small velocity. This velocity can be calculated from the diffusion coefficient according to Nernst's equation. Other considerations likewise lead to the conclusion that the colloidal particles have numerous charges†.

In the case of the alkaline solutions of the members of the lead type, it is evident from the diffusion data without further discussion that a colloid is present, since  $\text{Pb}(\text{OH})_2$  can only form ions with at most two charges. It is otherwise with polonium, the chemical properties of which are little known, and which can be present in solution in different electrolytic forms. Nevertheless a definite decision was possible when the sign of the charge on the polonium particles was determined. It was then found that in alkaline solution the great part of the polonium is charged negatively, in acid solution it is positively, and in neutral and very weakly acid solution it is predominantly negatively charged. If the negatively charged particles formed an electrolyte they must produce a complex anion, and such a solution can scarcely be as stable in presence of strong alkali as in weakly acid solution, since it has six charges—the minimum number which is compatible with any of the above given diffusion constants.

The diffusion constants calculated from the different layers show considerable variation. This is caused partly by the precipitation of some particles on the glass walls during

\* J. Billiter, *Zeit. phys. Chem.* iv. p. 365 (1906); Freundlich, *Kapillar-chemie*, p. 340.

† Smoluchowski, *Bull. de l'Acad. de Science de Cracovie*, p. 182 (1903); Zsigmondy, *Kolloidchemie* (Leipzig, 1912), p. 51.

diffusion, and is partly due to the fact that if one portion of a radioactive substance is in the ionic condition and the other part is in a colloidal state, then the velocity of diffusion calculated from the diffusing layers is not the resultant of the two diffusing velocities, but shows deviations from that which vary from layer to layer. For example, if a colloid with a velocity of 0.2 diffuses in a mixture with an electrolyte which has a velocity of 0.4 and if three colloidal particles are present for every ion, then after the diffusion has lasted three days we shall obtain the following constants:—

$$\text{I.} = 0.29 ; \quad \text{II.} = 0.24 ; \quad \text{IV.} = 0.25.$$

In a N/10 hydrochloric acid solution colloidal polonium particles are no longer detectable and the polonium diffuses with a velocity corresponding to a double charged ion.

Diffusion of polonium from N/10 hydrochloric acid solution into N/10 hydrochloric acid solution plus 5 per cent. ethyl alcohol.

		$D_{15^{\circ}5.}$	$D_{18^{\circ}.$
I.	$\frac{0.57}{2.83 \times 0.320} \dots\dots$	0.63	0.67
II.	$\frac{0.57}{2.85 \times 0.318} \dots\dots$	0.63	0.67
IV.	$\frac{0.57}{2.85 \times 0.314} \dots\dots$	0.63	0.67

After introducing the correction of 13 per cent. for the retarding influence of the alcohol, we have a diffusion constant of 0.77 sq. cm. per day, which corresponds to a double charged substance  $\text{PoCl}_2$ . More than 80 per cent. of this substance is dissociated into  $\text{Po}^{++}$  and  $\text{Cl}'$  ions in N/10 hydrochloric acid. Radium E takes up a mean position between polonium and radium D, and in N/1000 hydrochloric acid there are still colloidal radium E particles present although the ionic part of the substance predominates.

*On the Separation of Chemically identical Elements  
by means of Diffusion.*

The diffusion constants obtained for thorium B and radium D and for thorium X and radium, &c. show small differences (see table) which are ascribed to experimental errors. This raises the question whether identical elements of different atomic weights have the same diffusion coefficient, or whether it is possible to separate them from one another by long continued diffusion. To be able to answer

this question, which is of great theoretical interest, we must consider the factors that are operative in the diffusion of an ion in infinitely dilute solution.

We will compare the velocities of diffusion of two ions which have the same radius but different masses, understanding by "mass" the sum of the masses of the atom and its hydration molecules, and by "radius of the ion" the radius of the atom plus surrounding water molecules. Ions of chemically identical elements have the property that the radii of the atoms are equal\*, likewise their degrees of hydration, and only their masses, that is the masses of the nuclei, are different.

In comparing the diffusion velocities of such cases we have two extremes to consider. In the first case, the radius and the mass of the diffusing particles are very great in comparison with those of the molecules of the solvent, and the equation of Einstein and Smoluchowski † is valid, *i. e.*,

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r}.$$

The mass of the diffusing particles does not come in this formula, and the gravitational force vanishes compared with the osmotic force, and therefore in this extreme case the chemically identical elements must diffuse with exactly the same velocity in spite of the indifferent masses.

The other extreme case is, that the radius and the mass of the diffusing particles are very small in comparison with those of the solvent, and here, as in the case of diffusion of gas molecules in gases, the diffusion velocities are inversely proportional to the square root of the mass, and therefore we can expect a  $\frac{1}{2}$  per cent. difference in the diffusion constant for 1 per cent. difference in the atomic weight.

The case of the two chemically identical elements such as radium D and lead corresponds to neither of the above cases, since the mass and the radius are not so large relatively as demanded by the first case nor so small as required by the second case. However, it is much nearer those conditions for which the Einstein-Smoluchowski formula holds, in which the mass does not influence the velocity of diffusion, and therefore the possibility of separating chemically identical elements by diffusion liquid in solution is very slight.

In the case of the diffusion of these substances in the gaseous form, the second of the above considerations is

\* N. Bohr, *Phil. Mag.* Sept. 1913.

† A. Einstein, *Ann. der Physik*, xvii. p. 555 (1905).

applicable without further discussion, and here 1 per cent. difference in the atomic weights should produce a difference of  $\frac{1}{2}$  per cent. in the diffusion constant.

# SUMMARY.

(1) The valency of fifteen radio-elements has been determined by measuring their diffusion constants in acid solution. The valency thus measured directly agrees without exception with what would be expected from the character of the respective radio-elements determined by their non-separability from an element of known properties.

(2) Actinium sends triple charged ions into solution. This fact supports the view that actinium is the subsequent homologue of lanthanum.

(3) In alkaline solutions the short and long lived products of the emanation are present in a colloidal state, in agreement with the views of Paneth and Godlewski. Polonium, in very weakly acid and in neutral solution, is also present in a colloidal condition.

(4) The particles of the radio-colloids contain, in some cases, only two or three atoms.

(5) The possibility of separating chemically identical elements has been discussed.

My best thanks are due to Professor Sir Ernest Rutherford for the continued kind interest which he has taken in this research.

Manchester, August 1913.

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## LXVII. *The Absorption of $\gamma$ Rays.* By S. OBA, *Hon. Research Fellow, University of Manchester* \*.

IT is well known that with the usual experimental arrangements the absorption coefficient of the  $\gamma$  rays from radium decreases with increased thickness of absorber. This result has generally been ascribed to the heterogeneity of the primary rays. The softer constituents are supposed to suffer a greater amount of absorption and scattering, so that the beam as a whole becomes harder. It has also been observed that the  $\gamma$  rays scattered by matter are softer than the primary rays, and this result was explained by Florance † on the supposition that the softer constituents of the original  $\gamma$  rays are more easily scattered. Gray ‡, however, has

\* Communicated by Sir Ernest Rutherford, F.R.S.

† Florance, *Phil. Mag.* xx. p. 921 (1910).

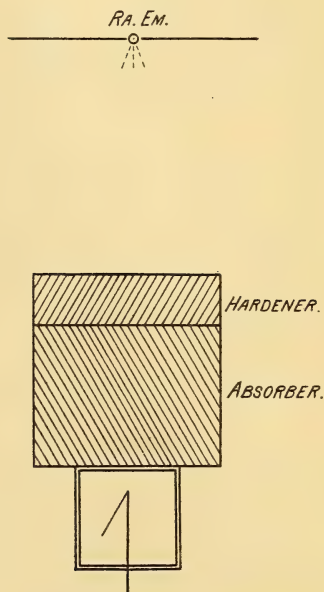
‡ Gray, *Phil. Mag.* xxvi. p. 611 (1913).



concluded that in the scattering of  $\gamma$  rays, the rays undergo a change in quality, becoming softer on scattering. The object of the present experiments was to try to investigate whether or not  $\gamma$  rays are changed in their quality by passing through matter. For this purpose the absorption by aluminium and iron was determined both for the primary  $\gamma$  rays of radium and for the rays after passage through different thicknesses of hardening materials such as copper, tin, and lead, since it is known that these metals apparently decrease the absorption coefficient in aluminium of  $\gamma$  rays which have passed through them.

The experimental arrangement is shown in fig. 1. The

Fig. 1.



$\gamma$  rays from the source of radium emanation in equilibrium with its products passed through the hardener and the absorber, aluminium or iron, and into the electroscope below. The radium emanation was enclosed in a small glass tube, and was suspended by strings 50 cm. above the middle of the electroscope. It could therefore be considered as a point source, and practically no correction was necessary for the oblique passage of the rays through the absorption-sheets. The absorbers and hardeners consisted of plates of equal size, 20 cm. square, projecting 4 cm. beyond the side walls of the electroscope. The hardeners were placed so as to rest on the absorber. The top of the electroscope was

closed by a thin sheet of the same material as the absorbing sheets. The walls and base, however, were of lead 9.5 mm. thick to keep out soft scattered radiations. The windows consisted of glass plates 8 mm. thick, which were protected by lead cylinders 9 mm. thick. A very small sulphur bead was used for the leaf-suspension, so that constant readings of the leak were obtained. The experiments were carried out in the centre of a large room, all substances from which scattered radiation might possibly arise being at least 2 metres distant from the electroscope.

The results are given in Tables I. and II. and shown in

TABLE I.—Al Absorbers.

Hardeners.	Values of $\frac{\mu}{D} \times 100$ .					
None .....	9.57	4.27	4.23	4.24	4.23	
2.4 cm. Cu.....	3.58	3.85	4.02	4.03	4.04	
2.5 cm. Sn.....	3.18	3.51	3.71	3.83	3.81	
2 cm. Pb.....	3.54	3.75	3.85	3.96	3.99	
1.1 cm. Pb.....	2.92	3.21	3.41	3.61	3.64	
2.0 cm. Pb.....	2.77	3.15	3.23	3.41	3.48	
2.9 cm. Pb.....	2.67	3.01	3.22	3.30	3.38	
3.8 cm. Pb.....	2.52	2.92	3.15	3.27	3.35	
Thickness of Absorbers,	2	3.4	6.6	9.8	13.0	16.2 cm.

TABLE II.—Fe Absorbers.

Hardeners.	Values of $\frac{\mu}{D} \times 100$ .							
None .....	4.53	4.28	4.20	4.13	4.02	3.95		
7.5 cm. Al.....	4.58	4.21	4.08	4.02	3.97	3.94		
2.4 cm. Cu.....	4.16	4.11	4.02	4.01	3.93	3.92		
2.5 cm. Sn.....	3.56	3.84	3.89	3.90	3.89	3.89		
2 cm. Pb.....	3.83	3.96	3.98	3.97	3.96	3.92		
1.1 cm. Pb.....	2.91	3.37	3.53	3.67	3.76	3.78	3.83	
2.0 cm. Pb.....	2.79	3.15	3.39	3.57	3.70	3.72	3.76	
2.9 cm. Pb.....	2.75	3.07	3.32	3.51	3.64	3.68	3.72	
3.8 cm. Pb.....	2.71	3.04	3.29	3.50	3.61	3.67	3.70	
Thickness of Absorbers,	2	1	2	4	6	8	10	12 cm.

figs. 2, 3, 4, and 5. Table I. refers to aluminium as absorber and Table II. to iron. The aluminium used was of density 2.70 and was practically pure; and for iron, sheets of mild steel of density 7.7 were used. In the first column of either table

Fig. 2.

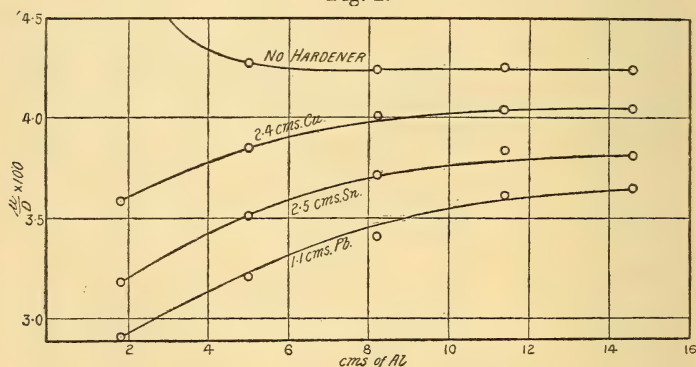
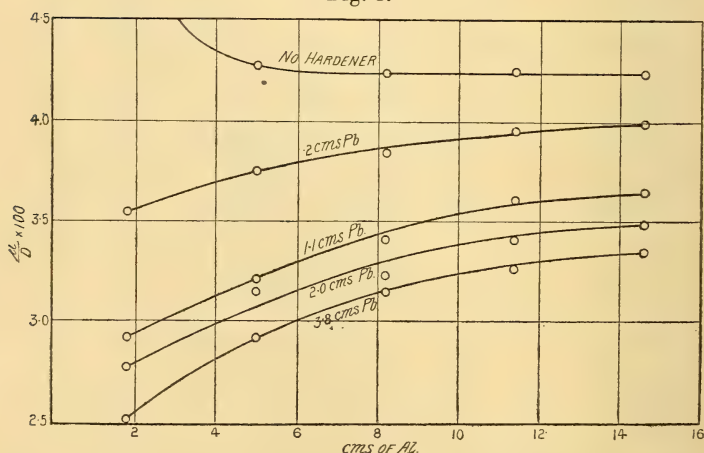


Fig. 3.



the material and thickness of the hardener are given. The thicknesses of 2.4 cm. copper, 2.5 cm. tin, 1.1 cm. lead were chosen, because they have about the same total absorption.

The remaining columns give the values of  $\frac{\mu}{D} \times 100$ , where  $D$  is the density of the absorber and  $\mu$  is the absorption coefficient calculated by the equation

$$I_1/I_2 = e^{\mu(x_2 - x_1)}.$$

In this equation  $I_1/I_2$  is the ratio of ionizations in the electro-scope when thicknesses  $x_1$  and  $x_2$  are used. The thicknesses are given in the bottom row of the tables.

Fig. 4.

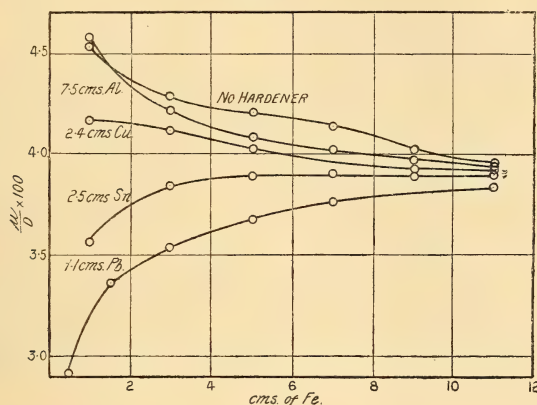
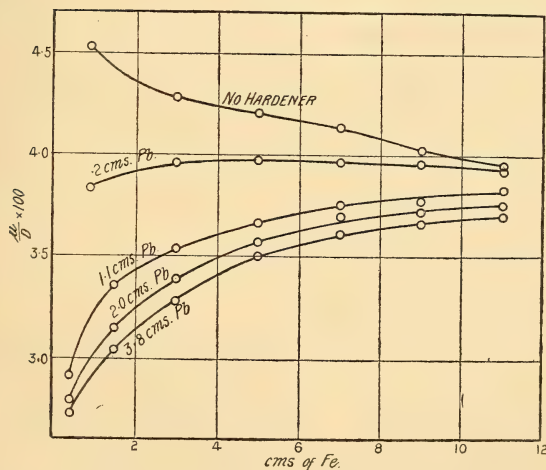


Fig. 5.



As will be seen from the curves, the results may be summarized as follows:—

(1) The absorption coefficient in aluminium for the primary  $\gamma$  rays decreases gradually with increasing thickness up to 6.6 cm. aluminium, and is then practically constant up to 16 cm., while that in iron continually decreases with increasing thickness.



(2) The material through which  $\gamma$  rays were first passed acts always to harden the rays. This is seen by the fact that the values for  $\mu/D$  given in the first row are always greater than those in the same column in any other row. The case of aluminium hardener for thicknesses of iron between .2 and 2 cm. appears an exception, but the difference in this case is almost within the experimental error.

(3) The decrease of the value of  $\mu/D$  becomes more pronounced for larger thicknesses of the absorber, but the decrease appears to tend to a limiting value. This result is seen from the value of  $\mu/D$  in the same column for different thicknesses of lead as hardener. This effect becomes more marked with increasing difference of atomic weights of the hardener and the absorber.

(4) The  $\gamma$  rays which have been hardened become gradually softer by passing through increased thickness of absorber. Moreover, particularly in the case of iron, it is possible that the hardened  $\gamma$  rays may tend with large thickness of absorber to the same penetrating power as that to which primary  $\gamma$  rays tend.

As has already been stated, the hardening of  $\gamma$  rays may be ascribed to the heterogeneity of the primary  $\gamma$  rays and a greater amount of absorption and scattering of the softer constituents. According to the analysis of Rutherford and Richardson\*, the  $\gamma$  rays dealt with in these experiments will be the easily absorbed rays from RaB with  $\mu = .51 \text{ cm.}^{-1}$  aluminium, and the penetrating rays from RaC with  $\mu = .115 \text{ cm.}^{-1}$  aluminium. After either 8.5 cm. aluminium, 1.5 cm. lead, 3.0 cm. iron, 2.7 cm. copper, or 3.3 cm. tin, the ionization due to RaB  $\gamma$  rays will be less than 1 per cent. of that due to the rays from RaC. We may consequently take these thicknesses as a measure of the range over which we may expect that hardening will be evident.

It will be seen, however, that the various effects cannot be completely explained as due to the soft radiations from RaB. For in the first place this will not explain the softening effect referred to in (4) above. Further, on such an hypothesis it follows that when the soft RaB rays are removed by absorption, the absorption coefficient of the remaining radiation should be the same and independent of the, so-called, hardener.

It must be remembered that the absorption coefficient  $\mu$  being calculated from the equation

$$I_1/I_2 = e^{\mu(x_2 - x_1)},$$

\* Rutherford & Richardson, *Phil. Mag.* xxv. p. 721 (1913).

the effects of both true absorption and scattering are superposed. However, it is generally supposed\* that the softer constituents of  $\gamma$  rays are more easily scattered than the harder ones, so that scattering gives no ready explanation of the softening obtained in these experiments.

It is possible that softening may be due in some way to the effect of excited  $\gamma$  rays in the absorption-sheets—*i. e.*, a transformation of part of the original  $\gamma$  rays. Such excited rays will be in all cases softer than the rays producing them, and the issuing rays will reach a state of equilibrium when the proportion of primary rays and of softer excited rays has a certain definite value. In the case of aluminium absorber, for example, when the rays have previously passed through a hardener of high atomic weight, they will have been robbed of the greater part of the soft constituents, so that as they pass through the aluminium more and more soft radiation will be excited until equilibrium is established. The absorption coefficient should therefore increase to a constant value. The numbers given in the tables tend to support this conclusion.

The question next arises as to whether, when this supposed equilibrium has been established, the absorption coefficient has the same value independent of the hardener. Leaving out of consideration the rays from RaB, this obviously ought to be the case if the rays from RaC are strictly homogeneous, *i. e.* consist of rays of one wave-length only. If the rays, for example, consist of two homogeneous beams of nearly equal wave-length, as the experiments of Moseley† suggest, the hardeners might be expected to show some selective effect which would permanently alter the absorption properties of the beam. The range of thickness used in these experiments is not large enough to decide the question definitely, although the results with Al appear to be in favour of the latter hypothesis.

In conclusion I desire to express my best thanks to Professor Sir Ernest Rutherford, at whose suggestion these experiments were carried out.

\* Florance, *loc. cit.*

† Moseley, *Phil. Mag.* xxvi. p. 1024 (1913).

LXVIII. *On the Integration of a Class of Ordinary Linear Differential Equations of the Second Order.* By HAROLD G. SAVIDGE \*.

THE class of equations to be considered may be expressed by the generalized equation :

$$\frac{d^2t}{dx^2} + 2P \frac{dt}{dx} + \left( P^2 + \frac{dP}{dx} - \frac{p^2 - \frac{1}{4}}{x^2} + qx^{m-2} - rx^{2m-2} \right) t = 0, \quad (1)$$

where  $m, p, q$ , and  $r$  are constants and  $P$  a function of  $x$ .

For the present we shall confine our attention to the following equation :

$$u'' + \left( \frac{1}{x} - 1 \right) u' + \left( \frac{a}{x} - \frac{n^2}{x^2} \right) u = 0, \quad \dots \quad (2)$$

dashes denoting differentiation with respect to  $x$ , and  $a$  and  $n$  being constants.

We shall define  $U_n(a; x)$  as a solution of this equation, and it will hereafter be shown how the equation (1) can be solved in terms of this function.

Formal solutions of equation (2) in convergent series of ascending powers of the argument can be obtained for all values of the constants  $a$  and  $n$ ; in particular finite solutions in terms of known functions can be obtained in the majority of those cases which will most frequently arise in practical problems; and the main object of this paper is to show at once the nature of these solutions and the substitutions in the variables necessary to lead to them. The series solutions can be written as follows :—

$$u_1 = \frac{x^n}{\Pi(2n)} \left[ 1 + \frac{n-a}{2n+1} \cdot \frac{x}{1} + \frac{(n-a)(n-a+1)}{(2n+1)(2n+2)} \cdot \frac{x^2}{2} + \dots \right] \quad \dots \quad (3)$$

$$u_2 = \frac{x^{-n}}{\Pi(-2n)} \left[ 1 + \frac{n+a}{2n-1} \cdot \frac{x}{1} + \frac{(n+a)(n+a-1)}{(2n-1)(2n-2)} \cdot \frac{x^2}{2} + \dots \right] \quad \dots \quad (4)$$

and (by the substitution  $u = e^x v$ )

$$u_3 (\equiv u_1) = \frac{x^n e^x}{\Pi(2n)} \left[ 1 - \frac{n+a+1}{2n+1} \cdot \frac{x}{1} + \frac{(n+a+1)(n+a+2)}{(2n+1)(2n+2)} \cdot \frac{x^2}{2} - \dots \right] \quad \dots \quad (5)$$

$$u_4 (\equiv u_2) = \frac{x^{-n} e^x}{\Pi(-2n)} \left[ 1 - \frac{n-a-1}{2n-1} \cdot \frac{x}{1} + \frac{(n-a-1)(n-a-2)}{(2n-1)(2n-2)} \cdot \frac{x^2}{2} + \dots \right] \quad \dots \quad (6)$$

\* Communicated by the Author.

These are two solutions, each written in two forms in order to show all cases where the series are finite. The case of zero factors in the denominators remains to be examined.

A constant has been introduced whereby simple relations hold between the functions for different values of  $a$  and  $n$ ; the following are for the series  $u_1$  and  $u_3$ ; the sign of  $n$  must be changed for the series  $u_2$  and  $u_4$ .

$$U_n(a-1; x) = \frac{1}{n-a} \left[ x U_n'(a; x) - a U_n(a; x) \right] \dots \dots \dots (7)$$

$$U_n'(a-1; x) = \frac{1}{n-a} \left[ (x-a) U_n'(a; x) + \left( \frac{n^2}{x} - a \right) U_n(a; x) \right] \dots \dots \dots (8)$$

$$U_n(a; x) = \frac{1}{n+a} \left[ x U_n'(a-1; x) + (a-x) U_n(a-1; x) \right] \dots \dots \dots (9)$$

$$U_n'(a; x) = \frac{1}{n+a} \left[ a U_n'(a-1; x) + \left( \frac{n^2}{x} - a \right) U_n(a-1; x) \right] \dots \dots \dots (10)$$

$$U_{n-\frac{1}{2}}(a-\frac{1}{2}; x) = x^{\frac{1}{2}} \left[ U_{n-\frac{1}{2}}'(a; x) + \frac{n}{x} U_n(a; x) \right] \dots \dots \dots (11)$$

$$U_{n-\frac{1}{2}}'(a-\frac{1}{2}; x) = x^{\frac{1}{2}} \left[ \left( 1 + \frac{2n-1}{2x} \right) U_{n-\frac{1}{2}}'(a; x) + \left\{ \frac{n(2n-1)}{2x^2} - \frac{a}{x} \right\} U(a; x) \right] \dots \dots \dots (12)$$

$$U_n(a; x) = \frac{x^{\frac{1}{2}}}{n+a} \left[ \left( 1 + \frac{2n-1}{2x} \right) U_{n-\frac{1}{2}}(a-\frac{1}{2}; x) - U_{n-\frac{1}{2}}'(a-\frac{1}{2}; x) \right] \dots \dots \dots (13)$$

$$U_n'(a; x) = \frac{x^{\frac{1}{2}}}{n+a} \left[ \frac{n}{x} U_{n-\frac{1}{2}}'(a-\frac{1}{2}; x) + \left\{ \frac{a}{x} - \frac{n(2n-1)}{2x^2} \right\} U_{n-\frac{1}{2}}(a-\frac{1}{2}; x) \right] \dots \dots \dots (14)$$

$$U_{n+1}(a; x) = \frac{1}{(n-a)(n+a+1)} \left[ (2n+1) U_n'(a; x) - \left\{ \frac{n(2n+1)}{x} + n-a \right\} U_n(a; x) \right] \dots \dots \dots (15)$$



$$U_{n+\frac{1}{2}}(a+\frac{1}{2}; x) = \frac{1}{n+a+1} \left[ x^{\frac{1}{2}} \left( 1 + \frac{2n}{x} \right) U_n(a; x) - U_{n-\frac{1}{2}}(a-\frac{1}{2}; x) \right] \quad \dots \quad (16)$$

$$U_n(a; x) = \frac{1}{n+a} \left[ (2a-1-x) U_n(a-1; x) + (n-a+1) U_n(a-2; x) \right] \quad \dots \quad (17)$$

$$U_{n+1}(a; x) = \frac{2n+1}{(2n-1)(n-a)(n+a+1)} \left[ U_{n-1}(a; x) + \left\{ \frac{2n(2a+1)}{2n+1} - \frac{2n(2n-1)}{x} \right\} U_n(a; x) \right] \quad \dots \quad (18)$$

A comparison of the series (3) and (5) shows that

$$U_n(-a-1; x) = (-1)^{-n} e^x U_n(a; -x). \quad \dots \quad (19)$$

*Solution in terms of Bessel Functions\*.*

If  $a = -\frac{1}{2}$ ,

$$u_1 = \frac{x^m}{\Pi(2n)} \left[ 1 + \frac{n+\frac{1}{2}}{2n+1} \cdot \frac{x}{1} + \frac{(n+\frac{1}{2})(n+\frac{3}{2})}{(2n+1)(2n+2)} \cdot \frac{x^2}{2} + \dots \right] \\ = e^{x/2} I_n\left(\frac{x}{2}\right) \times \frac{2^{2n} \Pi(n)}{\Pi(2n)} \quad \dots \quad (20)$$

[This may be verified by putting in equation (1)

$$m=1, \quad r=1, \quad q=0, \quad P=\frac{1}{2x}]$$

A second solution is given by substituting the Bessel function of the second kind,  $K_n$ , for  $I_n$ . Thus we have a complete solution in terms of these functions when  $a = -\frac{1}{2}$ ; and it may be obtained whenever  $2a$  is an integer (for any value of  $n$ ) by means of the relations (7) to (19).

*Solution when argument very great.*

When  $x$  is very great the series solutions given become laborious to calculate, and we may use the following asymptotic semi-divergent expansions in descending powers of the argument. (It will be noticed, from an examination of

\* Tables of  $I_n(x)$  are given in Gray & Matthews's 'Bessel Functions.'  $K_n(x)$  has been tabulated by Isherwood: Manchester Memoirs (1904), xlviii. p. 19.

the series (3) to (6), that the asymptotic value of all finite solutions is either  $u = x^a \times \text{constant}$ , or  $u = e^x x^{-a-1} \times \text{constant}$ .)

$$u_5 = x^a \left[ 1 + \frac{n^2 - a^2}{x[1]} + \frac{(n^2 - a^2)(n^2 - \{a-1\}^2)}{x^2[2]} + \dots \right] \quad (21)$$

$$u_6 = e^x x^{-a-1} \left[ 1 - \frac{n^2 - (a+1)^2}{x[1]} + \frac{(n^2 - \{a+1\}^2)(n^2 - \{a+2\}^2)}{x^2[2]} - \dots \right] \quad (22)$$

A comparison between these two series and the equations (3) to (6) and (20) shows that they satisfy the following relations for all the finite solutions (including those in terms of Bessel functions):—

$$u_1 = \frac{\cos(n-a)\pi}{\Pi(n+a)} u_5 + \frac{1}{\Pi(n-a-1)} u_6 \quad (23)$$

$$u_2 = \frac{\cos(n+a)\pi}{\Pi(-n+a)} u_5 + \frac{1}{\Pi(-n-a-1)} u_6 \quad (24)$$

*Second solution where  $u_2$  fails, — where  $2n$  is zero or a positive integer.*

If the equation  $u'' + Pu' + Qu = 0$  ( $P$  and  $Q$  functions of  $x$ ) has a known solution, say  $u_1$ , another solution is given by

$$u_1 \int \frac{e^{-\int P \cdot dx}}{u_1^2} dx^* \quad (25)$$

Thus when  $n=a$  we have a solution, on integrating by parts:

$$u_7 = -u_1 \text{Ei}(x) + e^x \sum_{s=0}^{s=2n-1} \frac{\Pi(2n-s-1)}{\Pi(2n)} x^{-n+s} \dagger. \quad (26)$$

(the symbol of summation being subject to the convention that as there are  $2n$  terms under it there are none when  $n=0$ ).

The corresponding solutions when  $n=a-1$ ,  $a-2$ , &c., may be found successively by application of the formulæ

\* See Forsyth's 'Differential Equations,' p. 110.

† The function  $\text{Ei}(x)$  or  $\int \frac{e^x}{x} \cdot dx$  has been fully tabulated by Glaisher (Phil. Trans. clx. (1870) p. 367).

(9), (17), which hold good for this solution. The result may be expressed generally as follows :

$$u_7 = e^x \sum_{s=0}^{s=2n-1} \left[ \frac{\Pi(a-n+s) \Pi(2n-1-s)}{\Pi(s) \Pi(a+n)} x^{-n+s} \right] - u_1 \text{Ei}(x) \\ - e^x \left\{ \frac{m_0 x^n}{|2n} - \frac{m_1 x^{n+1}}{|2n+1} + \frac{m_2 x^{n+2}}{|2n+2} - \dots \right\}. \quad (27)$$

where

$$m_0 = \int_0^1 \frac{x^{2n} - x^{n+a}}{1-x} \cdot dx, \quad \text{and}$$

$$m_1 = (n+a+1)m_0 - \frac{2n+2}{2n+1} \cdot \frac{(a-n)}{|1|},$$

$$2m_2 = (n+a+2)m_1 - \frac{2n+4}{2n+2} \cdot \frac{(a-n)(a-n-1)}{|2|},$$

$$3m_3 = (n+a+3)m_2 - \frac{2n+6}{2n+3} \cdot \frac{(a-n)(a-n-1)(a-n-2)}{|3|} \quad \&c.$$

When  $(a-n)$  is a positive integer, there are a finite number of these coefficients, the rest vanishing ; they may be expressed as follows :

$$m_0 = \sum_{s=1}^{s=a-n} \frac{1}{2n+s},$$

$$m_1 = (n+a+1) \sum_{s=2}^{s=a-n} \frac{s-1}{|1(2n+s)(2n+s+1)|},$$

$$m_2 = (n+a+1)(n+a+2) \sum_{s=3}^{s=a-n} \frac{(s-1)(s-2)}{|2(2n+s)(2n+s+1)(2n+s+2)|},$$

and so on.

(As before, it is to be understood that when the upper limit summation is less than the lower there no terms under the sign.)

If  $n+a$  is  $-1$  or less, the above constants are infinite ; in this case, and generally when  $a$  is less than  $-\frac{1}{2}$ , the following solution, which may be obtained as before, or immediately from the above by (19), is suitable :

$$u_8 = \sum_{s=0}^{s=2n-1} \left[ (-1)^{2n+s} \frac{\Pi(-n-a-1+s) \Pi(2n-1-s)}{\Pi(s) \Pi(n-a-1)} x^{-n+s} \right] - u_8 \text{Ei}(-x) \\ - \frac{p_0 x^n}{|2n} - \frac{p_1 x^{n+1}}{|2n+1} - \frac{p_2 x^{n+2}}{|2n+2} - \dots \quad (28)$$

where the constants  $p_0, p_1, \dots$  are obtained from  $m_0, m_1, \dots$  by substituting  $-(a+1)$  for  $a$  in the expressions determining the latter coefficients.

*Relations between  $u_7$ ,  $u_8$  and the other solutions.*

A comparison of  $u_8$  with  $u_5$  for all finite solutions shows that

$$u_5 = \frac{\cos 2n\pi}{\Pi(-n-a-1)} u_8,$$

or, what is the same thing,

$$u_8 = -\frac{\pi \operatorname{cosec}(\overline{n+a})\pi}{\Pi(n+a)} \cos 2n\pi \cdot u_5. \quad . \quad . \quad (29)$$

Also, by comparing the coefficients of  $x^n$  in  $u_1$ ,  $u_7$ , and  $u_8$ ,

$$u_7 = u_8 + u_1 \{ \pi \cot(\overline{n+a})\pi \}. \quad . \quad . \quad (30)$$

From these two we obtain

$$u_7 = -\frac{\pi \cot(\overline{n-a})\pi}{\Pi(n-a-1)} u_6 - \frac{\pi \sin(\overline{n+a})\pi}{\Pi(n+a)} \cos 2n\pi \cdot u_5. \quad (31)$$

When  $(a-n)$  is a positive integer the last reduces to

$$u_6 \cos(\overline{n-a})\pi = -\frac{u_7}{\Pi(a-n)}. \quad . \quad . \quad (32)$$

It should be noticed that in some cases the solutions  $u_5$  and  $u_6$  (21), (22) give at once two simple finite solutions equivalent to the above results.

The importance of these relations lies particularly in the fact that unless suitable solutions are selected, one degenerates virtually into a constant multiple of the other, the distinct solution appearing only as a relatively small error.

*Solutions in terms of Bessel functions.* [See (20).]

The following are the solutions in terms of Bessel functions when  $a = -\frac{1}{2}$ , 0,  $\frac{1}{2}$ , 1, and  $-1$ . The second solution is the corresponding expression having  $K_n(x)$  for  $I_n(x)$ .

$$U_n(-\tfrac{1}{2}; x) = \frac{2^{2n}\Pi(n)}{\Pi(2n)} e^{x/2} I_n(x/2),$$

$$U_n(0; x) = \frac{2^{2n-1}\Pi(n-\frac{1}{2})}{\Pi(2n)} e^{x/2} x^{1/2} [I_{n-\frac{1}{2}}(x/2) - I_{n+\frac{1}{2}}(x/2)],$$

$$U_n(\tfrac{1}{2}; x) = \frac{2^{2n}\Pi(n)}{\Pi(2n+1)} e^{x/2} [x I_{n-1}(x/2) - (2n-1+x) I_n(x/2)],$$

$$U_n(1; x) = \frac{2^{2n+1}\Pi(n+\frac{1}{2})}{\Pi(2n+2)} e^{x/2} x^{1/2} [(x+n-1) I_{n+\frac{1}{2}}(x/2) + (n+1-x) I_{n-\frac{1}{2}}(x/2)],$$

$$U_n(-1; x) = \frac{2^{2n-1}\Pi(n-\frac{1}{2})}{\Pi(2n)} e^{x/2} x^{1/2} [I_{n-\frac{1}{2}}(x/2) + I_{n+\frac{1}{2}}(x/2)].$$



Returning to the equation (1),

$$t'' + 2Pt' + (P^2 + P' - \frac{p^2 - \frac{1}{4}}{x^2} + qx^{m-2} - r^2x^{2m-2})t = 0. \quad (1)$$

Putting  $t = x^{\frac{1}{2}} \exp. \left\{ -\int (P + rx^{m-1}) dx \right\} u$   
and substituting,

$$\frac{d^2u}{dx^2} + \left( \frac{1}{x} - 2rx^{m-1} \right) \frac{du}{dx} + u \left\{ (q - mr)x^{m-2} - \frac{p^2}{x^2} \right\} = 0,$$

and on putting in this equation  $X = \frac{2r}{m} x^m$

we obtain

$$\frac{d^2u}{dX^2} + \left( \frac{1}{X} - 1 \right) \frac{du}{dX} + u \left( \frac{a}{X} - \frac{n^2}{X^2} \right) = 0,$$

where  $a = \frac{q}{2mr} - \frac{1}{2}, \quad n = \frac{p}{m}.$

This is the equation (2), and the solution of (1) may be written

$$t = x^{\frac{1}{2}} \exp. \left\{ -\int P \cdot dx - \frac{rx^m}{m} \right\} U_{p/m} \left( \frac{q}{2rm} - \frac{1}{2}; \frac{2r}{m} x^m \right).$$

The following are some of the principal forms comprised in the equation. In the following  $b, c, f, g, h, k, l$  are constants, in addition to  $m, p, q, r.$

$$(1) \quad t'' + 2ct' - t \left\{ \frac{p^2 - \frac{1}{4}}{x^2} - (c^2 + q) + r^2x^2 \right\} = 0.$$

Solution :

$$t = x^{\frac{1}{2}} \exp. \left( -cx - \frac{rx^2}{2} \right) U_{p/2} \left( \frac{q}{4r} - \frac{1}{2}; rx^2 \right).$$

$$(2) \quad t'' + \left( \frac{2b}{x} + 2cx \right) t' + t \left\{ \frac{(b - \frac{1}{2})^2 - p^2}{x^2} + (q + 2bc + c) + (c^2 - r^2)x^2 \right\} = 0.$$

Solution :

$$t = x^{\frac{1}{2}-b} \exp. \left( -\frac{r+c}{2} x^2 \right) U_{p/2} \left( \frac{q}{4r} - \frac{1}{2}; rx^2 \right).$$

$$(3) \quad t'' + (2bx + 2c)t' - t(gx^2 + 2hx + k) = 0.$$

Solution :

$$t = (x+f)^{\frac{1}{2}} \exp. \left\{ -\frac{b+r}{2} (x+f)^2 + l(x+f) \right\} U_{\frac{1}{2}} \left\{ a; r(x+f)^2 \right\},$$

where

$$a = \frac{lc + hf - k - b}{4r} - \frac{1}{2}, \quad r = \sqrt{b^2 + g}, \quad f = \frac{bc + h}{r^2}, \quad l = \frac{bh - cg}{r^2}.$$

$$(4) \quad t'' + \left( \frac{2b}{x} + 2c \right) t' + t \left\{ \frac{(b - \frac{1}{2})^2 - p^2}{x^2} + \frac{2bc + q}{x} + (c^2 - r^2) \right\} = 0.$$

*Solution :*

$$t = x^{\frac{1}{2}-b} \exp. \{ -(c+r)x \} U_p \left( \frac{q}{2r} - \frac{1}{2}; 2rx \right).$$

$$(5) \quad t'' + \left( \frac{2b}{x} + \frac{2c}{x^2} \right) t' + t \left\{ \frac{(b - \frac{1}{2})^2 - p^2}{x^2} + \frac{2bc + q - 2c}{x^3} + \frac{c^2 - r^2}{x^4} \right\} = 0.$$

*Solution :*

$$t = x^{\frac{1}{2}-b} \exp. \left( \frac{c-r}{x} \right) U_p \left( \frac{q}{2r} - \frac{1}{2}; \frac{2r}{x} \right).$$

$$(6) \quad t'' + 2cx^2t' + t \{ (2c+q)x + (c^2-r^2)x^4 \} = 0.$$

*Solution :*

$$t = x^{\frac{1}{3}} \exp. \left\{ -(c+r) \frac{x^3}{3} \right\} U_1 \left( \frac{q}{6r} - \frac{1}{2}; \frac{2rx^3}{3} \right).$$

$$(7) \quad (b+x)t'' + (c+2fx)t' - (g+hx)t = 0.$$

*Solution :*

$$t = (b+x)^n \exp. \left\{ -(f+r)(b+x) U_n \left( \frac{q}{2r} - \frac{1}{2}; 2r(b+x) \right) \right\},$$

where  $n = bf - \frac{c-1}{2}; \quad r = \sqrt{f^2 + h}; \quad q = bh + 2bf^2 - cf - g.$

$$(8) \quad t'' + (2b + 2c\epsilon^{mx})t' + t(f + g\epsilon^{mx} + h\epsilon^{2mx}) = 0.$$

*Solution :*

$$t = \exp. \left( -bx - \frac{c+r}{m} \epsilon^{mx} \right) U_{p/m} \left( \frac{q}{2rm} - \frac{1}{2}; \frac{2r}{m} \epsilon^{mx} \right),$$

where  $r = \sqrt{c^2 - h}; \quad p = \sqrt{b^2 - f}; \quad \text{and} \quad q = g - cm - 2bc.$

$$(9) \quad \log x \cdot t'' + \frac{2b}{x} t' + \frac{c}{x^2} t = 0.$$

*Solution :*

$$t = (\log x)^{\frac{1}{2}-b} U_{b-\frac{1}{2}} \left( b + c - \frac{1}{2}; \log x \right).$$

Note :—When  $m=0$  the solution of (1) is

$$t = \exp. (-\int P \cdot dx) x^{\frac{1}{2} \pm \sqrt{p^2 + r^2 - q}},$$

and when  $r=0$  the solution is

$$t = x^{\frac{1}{2}} \exp. (-\int P \cdot dx) J_{2p/m} \left( \frac{2q^{\frac{1}{2}} x^{m/2}}{m} \right)^*.$$

January, 1914.

LXIX. On *Wien's Law*. By R. HARGREAVES, M.A.†

**W**IEN'S Law has been approached in a variety of ways, but the arguments usually lack some element of generality as regards the shape of enclosure or type of motion. It is proposed to deal here with the mean effect for an enclosure of any shape, in which each element  $dS$  of surface has an arbitrary normal component  $w$  of small motion.

In the element of time  $dt$  a change of wave-length affects the radiation in a small part of the whole volume proportional to  $dt$ , and this is exactly representative of the action to which radiation from every part of the interior will in turn be exposed. The primary effect  $\frac{\Delta \lambda}{\lambda} = \frac{2w \cos i}{V}$ , with  $i$  for angle of incidence, is to be modified by taking into account the ratio of the volume affected in time  $dt$  to the total volume, and also a mean is to be taken for various angles of incidence. The resulting mean is

$$\frac{\Delta \lambda}{\lambda} = \int_s \int_0^{\frac{\pi}{2}} \frac{2w \cos i}{V} \cdot \frac{dS V dt \cos i}{2v} \cdot \sin i \, di = \int_s \frac{w \, dt \, dS}{3v} = \frac{\Delta v}{3v}. \quad (1)$$

Here  $dS \cdot V dt \cos i$  is the volume from which radiation reaches the surface in time  $dt$  at angle  $i$ , and half of this volume is taken because only the half of the radiation which is *approaching*  $dS$  is affected by the change. The factor  $\sin i \, di$  is used to average the effects for various angles of incidence, and as the integral of  $\sin i \, di$  is 1, it is not necessary to write this integral in the denominator.

\* Tables of this function appear in Gray & Matthews's 'Bessel Functions,' and the Bessel function of the second kind  $Y$  furnishing the second solution in this case has been tabulated by B. A. Smith (Messenger of Mathematics, xxvi. p. 98).

Two other known functions,  $\int e^{-x^2} \cdot dx$  (the probability integral), and  $\int e^{x^2} \cdot dx$ , tabulated by H. G. Dawson (Proc. Lond. Math. Soc. xxix. p. 519, 1898), occur when  $4n$  is an odd integer. [See (25).]

† Communicated by the Author.

The use of (1) with  $p=E/3v$  makes

$$dE + pdv = dE + \frac{E dv}{3v} = dE + \frac{E d\lambda}{\lambda},$$

or 
$$\frac{dE + pdv}{\theta} = \frac{d(E\lambda)}{\lambda\theta} = dS, \text{ say ; } \dots (2)$$

and if this is a true differential, then  $E\lambda$  and  $S$  are functions of  $\lambda\theta$  or  $x$ , and  $x=\text{constant}$  is the adiabatic relation. The above is applicable to monochromatic radiation, or to radiation within the range of an element  $d\lambda$ .

It is desirable to show the factor  $v$  explicitly in  $E$ , and for that purpose we note that  $v/\lambda^3$  is constant or that  $v d\lambda/\lambda^4$  is constant ; *i. e.*, in presenting the part of energy attaching to a range  $d\lambda$ , we must count  $d\lambda$  as susceptible of change in the same proportion as  $\lambda$  in connexion with change of volume. Thus we are led to the forms

$$E = \frac{v d\lambda}{\lambda^4} \cdot \frac{\phi(x)}{\lambda}, \quad S = \frac{v d\lambda}{\lambda^4} \psi(x), \quad \text{with } \frac{d\psi}{dx} = \frac{1}{x} \frac{d\phi}{dx} \dots (3)$$

For example, with Planck's law  $\phi = 1/(e^{c/x} - 1)$ , and then

$$\psi = \frac{e^{c/x}}{x(e^{c/x} - 1)} - \frac{1}{c} \log(e^{c/x} - 1),$$

apart from a constant multiplier in each case.

The above statement turns on two means expressed respectively by  $p=E/3v$  and  $\Delta\lambda/\lambda=\Delta v/3v$ , which are found in very similar ways. The element of work is in fact

$$\begin{aligned} p\Delta v &= \int_s \int_0^{\frac{\pi}{2}} \frac{E}{v} \cdot w \cos i \, dt \cdot dS \cos i \cdot \sin i \, di \\ &= \int_s \int_0^{\frac{\pi}{2}} \frac{2w \cos i}{V} \cdot \frac{V \, dt \cos i \, dS}{2v} E \sin i \, di = \frac{E\Delta v}{3v}, \quad \dots (4) \end{aligned}$$

an exact counterpart of (1). Thus we have  $p\Delta v=E\Delta\lambda/\lambda$  immediately without performing the integration ; and in fact (2) is valid for radiation in two dimensions or in one. It is essential to both arguments that energy-content should in respect to all wave-lengths be uniform throughout the volume.



LXX. *On the Action of Colloids on Radioactive Products in Solution.* By T. GODLEWSKI, Ph.D., Professor of Physics, Technical High School, Lemberg (Lwów)\*.

1. *The Radioactive Hydrosols.*

IN a previous paper, "On Solutions of Radioactive Products" †, it was shown that the products of the active deposit of radium in neutral, alkaline, or weakly acidulated solutions are in the colloidal state. This conclusion was based upon the results derived from an investigation of the electrolysis of aqueous solutions of radium emanation together with its successive products. The experiments established the fact that in acidulated solutions or in presence of polyvalent cations, the said products are deposited at the cathode almost exclusively. On the other hand, in alkaline solutions or in presence of polyvalent anions, it was the anode which first of all was activated by electrolysis. Now precisely this change of sign of the electric charge under the influence of H, OH, or polyvalent ions constitutes the property characteristic ‡ of colloidal suspensions, and it strongly suggests that we are dealing here with a process of the nature of cataphoresis and with colloidal hydrosols. When it is remembered, indeed, that the above-mentioned products are but very sparingly soluble in water, we easily understand that an atom of RaA arising from an atom of emanation dissolved in water, and thus suddenly appearing in a medium which does not dissolve RaA, will constitute a nucleus for the centre of the distinct phase. In Zsigmondy's § opinion, the most satisfactory method for the production of colloids is to induce reactions from which there shall result the formation of substances which, as crystalloids, are insoluble in the medium. In the case of usual irreversible colloids, *e. g.* those of metals, this result can be arrived at either by producing a suitable reduction in the liquid medium or by pulverization of the metals attended by a supply of electrical energy (Bredig's or Svedberg's method). In the case of radioactive products, the reaction which produces centres of colloidal suspensions is the radioactive transformation itself, whence new atoms come into being.

\* Communicated by the Author. Presented before the Academy of Sciences in Cracow at the sitting of 5th January, 1914.

† T. Godlewski, *Bull. Intern. de l'Acad. d. Sc. de Cracovie*, 1913, p. 335; *Le Radium*, 1913, p. 250.

‡ Cassuto, 'Der Kolloide Zustand der Materie,' p. 245.

§ Zsigmondy, 'Kolloidchemie,' p. 2.

Almost at the same time, but by a different method, Paneth\* arrived independently at closely similar conclusions concerning the state of radioactive products in solution. He found that it was possible to separate polonium from lead by means of a process of dialysis. In the process the lead was shown to pass through parchment or animal membrane, while the polonium remained. These results were strikingly confirmed by the subsequent investigations of Paneth† and Hevesy‡. They, too, have observed a change of direction in the migration of certain radioactive products (ThB and Po), according as the solution was acidulated or alkaline. They determined, moreover, the coefficients of diffusion of these products, and found them considerably smaller (especially in alkaline solutions) than might have been anticipated from the valency of these elements. Hence the order of magnitude of these colloidal radioactive suspensions becomes approximately calculable, and the writers quoted found that the suspensions consist of no more than 8-3 or 2 atoms. According to this, solutions of radioactive products form a transition between ordinary colloidal and ionic solutions.

If it is thus conceded that the centra of colloidal radioactive suspensions consist of aggregations of atoms, we can then easily explain an observation previously made by the writer. In the above-mentioned paper it was shown that by means of electrolysis of pure water saturated with radium emanation together with its successive products, the following deposits on the electrodes were obtained:—On the anode, RaA and about one-third of the equivalent quantity of RaC; on the cathode, RaB and about one-third of the equivalent quantity of RaC. In pure water RaA is deposited only on the anode, *i. e.*, it forms negative hydrosols; RaB appears only at the cathode, *i. e.*, it forms only positive hydrosols. The question arises, What does the fact mean, that RaC is deposited in the same solution equally well at the cathode as at the anode? Must it be supposed to form positive hydrosols or negative ones?

In order to elucidate this question, let us assume that RaC in pure water gives rise to negative hydrosols, just as RaA does. If the centre of the suspension of RaA consists of an aggregation of several atoms, we easily see that as soon as one of these is transformed into RaB, this

\* Paneth, *Wien. Sitzber.* cxxi. p. 2193, cxxii. p. 1079; *Kolloid-Zeitschr.* xiii. p. 1.

† Paneth, *Kolloid-Zeitschr.* xiii. p. 297.

‡ Hevesy, *Phys. Zeit.* xiv. 1913, p. 1202.

newly-formed atom will readily be expelled from the aggregate on account of the reaction following upon the emission of an  $\alpha$  particle. In consequence of this, the groups of hydrosols of RaA, travelling towards the anode, will contain only atoms of RaA, and they will not carry with them atoms of RaB. The latter, after suitable coagulation, will produce positive hydrosols and will deposit them at the cathode.

It is otherwise with RaC. When the atom of RaC arises from RaB the reaction is extremely feeble, RaB emitting only the  $\beta$  particle. For this reason, if one of the atoms in the aggregate RaB which forms the centre of a positive hydrosol, is transformed into RaC, it will not escape from its environment of remaining RaB atoms, which form a positive hydrosol, but will be carried with them to the cathode. We then get an aggregate similar to that which is obtained by mixing two colloids of opposite signs when one of the two is in considerable excess. In this case no precipitation occurs, but the colloid which is in small quantity becomes oppositely electrified, taking the charge of the colloid which is in excess\*. Something of the kind takes place here. We may therefore expect that those RaC atoms only go to the anode which during their transformation managed to escape from the aggregate RaB; and also those which belong to groups in which the majority of the RaB atoms have already undergone transformation. The groups in which so many RaC atoms have arisen that through their presence the charge of the remaining RaB atoms has become neutralized, must be precipitated: they may become fixed to the walls of the vessel; at any rate they are not carried with the electric current. The groups containing an excess (with respect to charge) of RaB over RaC will go to the cathode. Then follows the appearance of RaC at the cathode, though it forms negative hydrosols.

The results of further investigation on the subject of the action of colloids on radioactive products in solution confirm abundantly the hypothesis which has here been brought forward.

## 2. Interaction of Colloids.

After establishing that radioactive products in solution are in the colloid state, I investigated the influence of foreign colloids upon these products. This subject has hitherto received but scant attention: we can only mention one

\* Zsigmondy, 'Kolloidchemie,' p. 58.



elaborate paper, published by Miss Fellner, "Ueber die Adsorption radioaktiver Substanzen durch Kolloide"\*. Miss Fellner carefully investigated the adsorption of certain radioactive products by colloidal silicic acid. She found that many products undergo considerable adsorption by this hydrosol, so that it is possible to concentrate them by this means. We may also note the researches of Szillard† on the adsorption of UrX, and a new method of concentrating this substance. Here we must also remark that more than two years before my work and that of Paneth was published, Szillard, whilst investigating the nature of reactions of radioactive products, pointed out that they may be considered as interactions of ions and electrified suspensions, or, generally speaking, between electrified bodies on each other. The mutual interaction between colloids is a typical instance indeed of such a phenomenon.

Starting from the assumption that radioactive products in water form colloidal hydrosols, we have to expect that the action of foreign colloids upon them will follow the well-known laws‡ of interaction between colloids.

Colloids, when of opposite sign, precipitate each other. From the researches of Biltz§ we know that this mutual precipitation of colloids of opposite sign is limited by certain conditions as to the quantities of both colloids present. For every pair of colloids an "optimum" can be found corresponding to the equalization of electric charges, which is accompanied by complete precipitation. Thus there exists a certain range of concentrations within which mutual precipitation takes place, the range which (*e. g.* in the case of pigments) is the narrower || as the diffusibility of pigment is less. If the degree of concentration of one colloid is far outside the limits alluded to, no precipitation occurs, but owing to ordinary and also to electrical adsorption the colloid which is present in considerably smaller quantity will gain (from the other) an opposite charge, so that both colloids will travel in the same direction in the electric field.

The influence exerted by ordinary colloids on radioactive products in solution has been examined by the writer, first of all by means of observing the course of electrolysis.

\* Miss Fellner, *Zeit. f. anorg. Chemie*, lxxiii. p. 1.

† Szillard, *Compt. Rend.* 1909; *Le Radium*, 1909, p. 80, and 1910, p. 366.

‡ See, for example, Zsigmondy, 'Kolloidchemie,' pp. 52, 220.

§ Biltz, *Ber. d. deut. chem. Ges.* Band xxxvii. 1907, p. 1095.

|| Zsigmondy, *loc. cit.* p. 221.



Various colloids, in different, accurately known quantities, were added to water which was saturated with radium emanation and its successive products. The solution was then electrolysed between platinum electrodes, a P.D. of 220 volts being employed. The experimental arrangements used in this part of the work were the same as those described in my previous paper\*. The  $\alpha$  activity of the electrodes was determined after the electrolysis by means of a quadrant electrometer; the measurements were subsequently repeated, in order to identify the deposited products. The activity is expressed below in arbitrary units, which, however, are invariably the same throughout this paper. The water used in these experiments was obtained by distillation from ordinary distilled water, a quartz condenser being employed.

### 3. *The Influence of Negative Colloids on Radium Products in solution.*

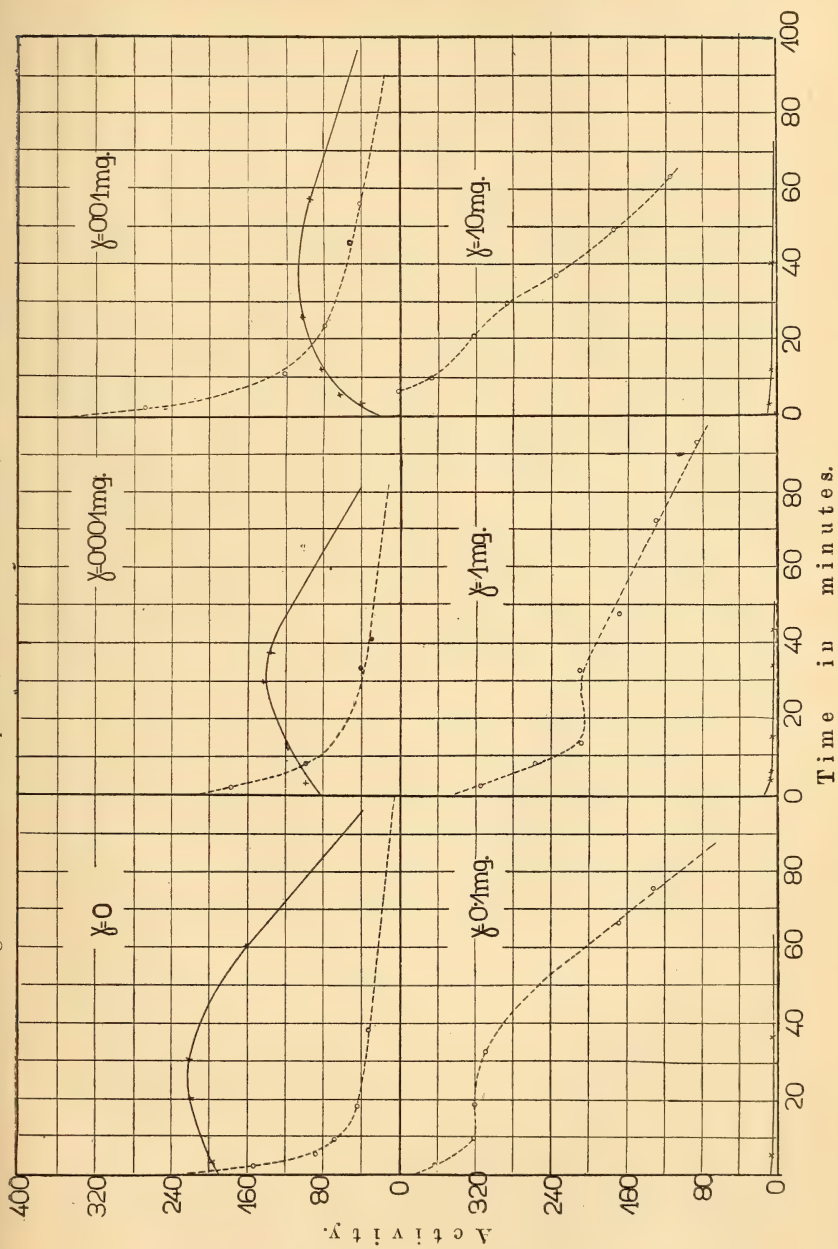
*Experiments with arsenious sulphide.*—Colloidal arsenious sulphide was obtained in the usual way, *i. e.*, by passing a stream of gaseous hydrogen sulphide through a dilute solution of arsenious acid. After driving off the remainder of hydrogen sulphide and filtering, a solution was obtained which in flasks of Jena glass could be preserved for weeks. The solution was suitably diluted, and 1 cm.<sup>3</sup> of variable concentration ( $\gamma$ ) was added to 16 cm.<sup>3</sup> of water saturated with radium emanation. The results of measurements of the activity of both electrodes and its variation in time are plotted in fig. 1. The continuous curve on the figure refers to the cathode, the dotted one to the anode.

It will be noticed that the influence of arsenious sulphide on the result of electrolysis is very marked; the direction of the variation is that which was to be expected on account of the sign of the colloid.

When this negative hydrosol is added, the amount of products deposited at the cathode decreases at first. The decrease of the maximum ordinates of the continuous curves points to a diminution of the amount of RaB with increasing concentration of arsenious sulphide; the diminution of the initial ordinates indicates a decrease of the quantity of RaC deposited at the cathode. The continuous curves on fig. 1 show that when arsenious sulphide is used in feeble concentration, the quantity of RaC deposited at the cathode decreases, but the relative amount of  $\frac{\text{RaB}}{\text{RaC}}$  at first must increase. This

\* Godlewski, *loc. cit.*

Fig. 1. (Arsenious Sulphide.) — Cathode; --- Anode.



fact seems to confirm our hypothesis concerning the appearing of RaC at the cathode. If it is true indeed that RaC only travels to the cathode if carried along by the RaB atoms which remain in the positive colloidal agglomerate, this aggregate must have a smaller positive charge than one consisting solely of RaB atoms. The compound hydrosols (containing RaB and RaC) will thus be more easily precipitated, and precipitation will occur at a lower concentration of arsenious sulphide. At the cathode, therefore, with the concentration, *e. g.*  $\gamma = 0.01$  mg., we get almost pure RaB.

It is only with concentrations ten times stronger, or more, that the characteristic change of sign and the traction of RaB towards the anode occurs. The almost horizontal trend of the dotted curve (fig. 1), corresponding to times from 15 to 35 min., proves unmistakably the appearance of RaB at the anode. For this, as well as for all higher concentrations, we observe that all the products (RaA, RaB, RaC) are deposited at the anode. In accordance with what the theory of colloids demands, the products are adsorbed by the colloid of opposite sign, which is present in great excess.

From an inspection of the figure, we conclude that at concentrations at which RaB appears at the anode the activity of the cathode is exceedingly feeble, and falls in presence of greater concentrations of arsenious sulphide to below 1 per cent.

*Experiments with colloidal platinum.*—Colloidal platinum was prepared by Bredig's well-known method, *i. e.*, by pulverization of platinum in an electric arc. The chief solution contained 7.6 mg. platinum in 100 cm.<sup>3</sup>. Certain quantities of that solution were added to 16 cm.<sup>3</sup> of water saturated with radium emanation; the resulting solution was electrolysed during 90 sec., under the same conditions as heretofore. The results of these experiments are shown in fig. 2.

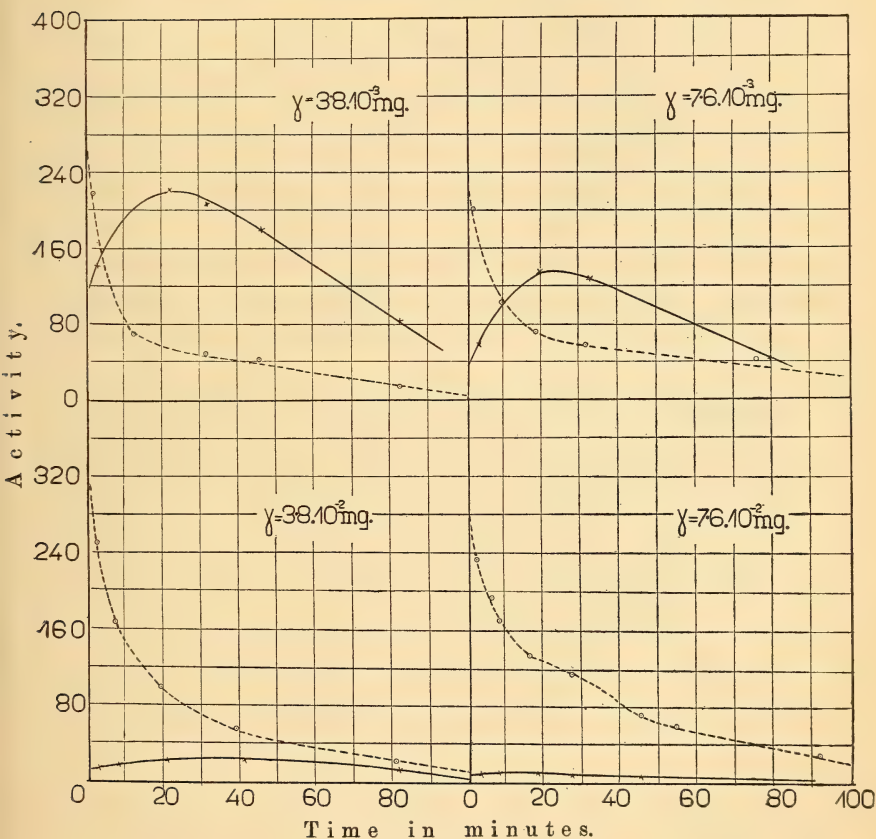
From the curves we see that the influence of platinum is the same as that of arsenious sulphide. Small quantities produce a decrease of activity of the cathode, and (as before) the quantity of RaC deposited at the cathode is the first to decrease. It is thus seen that the positive sols, containing RaC along with RaB, are precipitated first as if they had a lower charge.

In the presence of still greater concentrations RaB also disappears from the cathode; at a yet higher concentration, when the activity of the anode is exceedingly feeble, RaB appears at the anode. The positive hydrosols become now negatively charged, all the products being deposited at the anode.

Similar experiments with colloidal gold obtained by Bredig's method have led to precisely the same results.

Fig. 2. (Platinum.)

— Cathode ; - - - - - Anode.



We may therefore conclude that the addition of a negative colloid in small quantity makes the products deposited at the cathode to diminish in amount and afterwards to disappear ; that is to say, it produces the precipitation of colloids of opposite signs. In the presence of still greater quantities of negative colloids the positive products become negatively charged, and they are then deposited at the anode : we have thus before us a case of adsorption by a colloid being used in great excess.



4. *Influence of Positive Colloids.*

The positive colloid employed was a dialysed solution of ferric oxide; it was the ordinary commercial article, containing 6.62 gr. of ferric oxide per 100 cm.<sup>3</sup> The experiments were conducted on the same lines as before; their results are plotted in fig. 3.

It will be seen that the influence of colloidal ferric oxide is quite special. As the theory of colloids might lead us to expect, the amount of products (RaA and RaC) deposited at the anode decreases at first: thus giving evidence of the precipitation of oppositely electrified hydrosols. In certain experiments a slight diminution of the quantity of RaC deposited at the cathode was noticeable in the low concentrations, while the relative amount  $\frac{\text{RaB}}{\text{RaC}}$  increased to a small

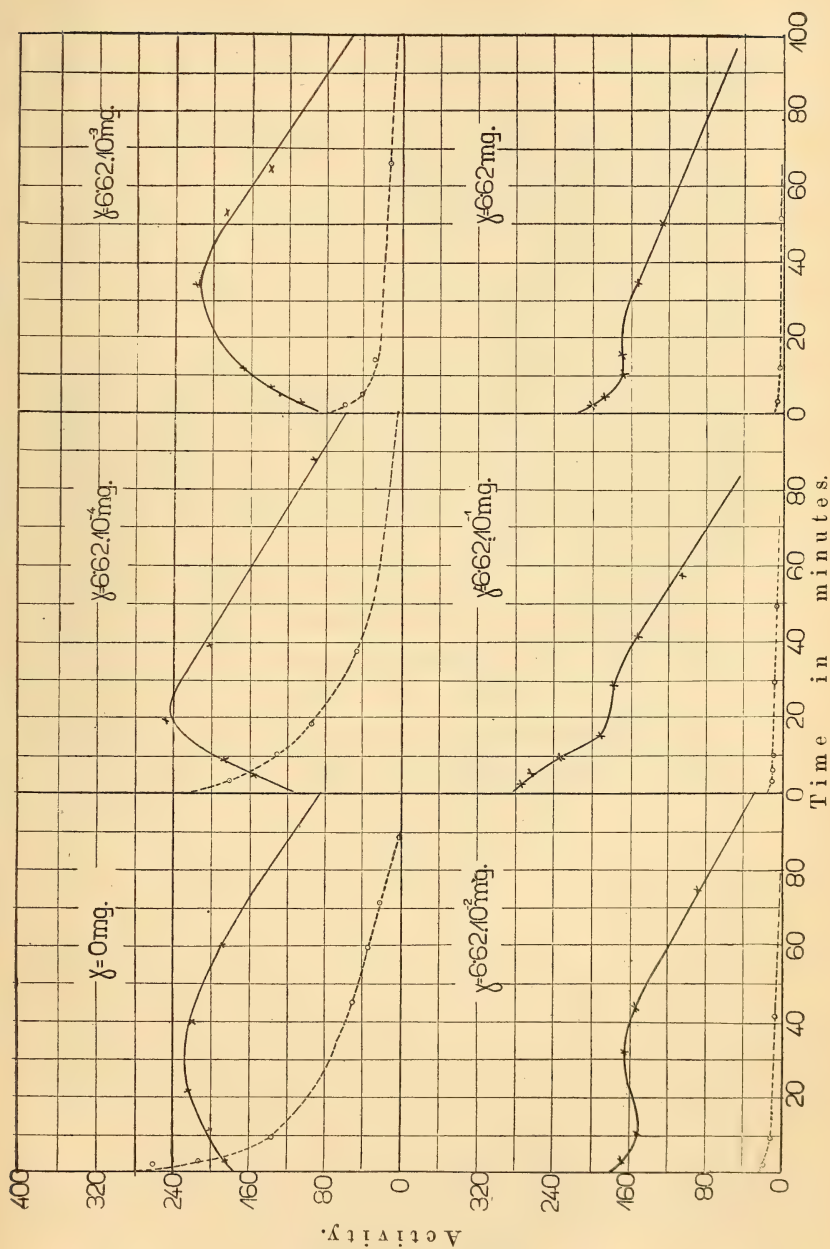
extent. This result may perhaps be ascribed to a greater adsorption of RaC by ferric oxide than by the remaining atoms of RaB.

In concentration  $\gamma = 6.6 \cdot 10^{-3}$  mg. we observe a very great falling off in the activity of the anode; with a higher concentration the activity of the anode is exceedingly slight. On the other hand, from the concentration  $\gamma = 6.6 \cdot 10^{-2}$  mg. upwards the appearance of RaA and RaC at the cathode is manifest, so that all the products are deposited at this electrode. In these concentrations, then, the products which usually form negative hydrosols become positively electrified and are deposited at the cathode.

The conclusive method of proving the adsorption of negative hydrosols is to add ferric oxide in considerable quantity to water freshly saturated with emanation and to proceed with the electrolysis as rapidly as possible. The deposit at the cathode in this case will be found to consist of almost pure RaA.

It may be added that the results adduced in the foregoing pages have been found in each case by taking average values out of a large series of individual measurements. Though the sequence of the curves (corresponding to various concentrations) in different experiments was always the same, the particular results were observed to be subject to some slight variations, especially at lower concentrations. Subsequently it was found that slight alteration of the circumstances of the experiment (as for instance a change in the rapidity of mixing, variation of the rate at which the colloid was supplied, and even the concentration at which a given quantity of colloid was added)—all this exercises a considerable effect on the result obtained. In order to arrive

Fig. 3. (Ferric oxide.) — Cathode; - - - - Anode.



at identical curves it was necessary, especially in the case of low concentrations, to keep all external conditions of individual experiments exactly alike. Similar facts have been observed in dealing with the precipitation of ordinary colloids\*.

Leaving aside these details we may conclude by saying that ferric oxide, and generally speaking all positive colloids, when added in relatively small amount, conduce to precipitation of RaA and RaC, which are among negative colloids; in higher concentrations positive colloids adsorb them, thus inverting their signs. This action is therefore exactly opposite to that of negative hydrosols, as was of course to be foreseen from theory.

#### 5. *Precipitation of Radioactive Products with Colloids.*

The experiments heretofore described show that relatively small quantities of colloids are able to adsorb all the products contained in a solution. The question now arises: In how far are the compounds of colloids with radioactive products stable? In order to elucidate this point the following experiments were made.

To 16 cm.<sup>3</sup> of water saturated with radium emanation a few milligrams of colloidal arsenious sulphide, platinum or gold were added; the latter was obtained either by Bredig's method or by that of Zsigmondy†; after which the colloids were precipitated, using a small amount of aluminium sulphate solution.

The precipitate collected on a small filter was tested as to activity immediately after desiccation. It was found that all the products (RaA, RaB, and RaC) were present on the filter; and further, that by means of one such single precipitation it was possible to separate the products almost quantitatively, so that the filtered liquid contained scarcely any product.

It was likewise possible to collect by the same method the radioactive products on positive hydrosols *e.g.* on ferric oxide. A greater amount of this hydrosol, however, was required in order to effect the adsorption; besides, this colloid owing to greater voluminousness is much more slowly filtered; hence such colloids as gold or platinum are more suitable when it is desired to concentrate radioactive products.

By the use of these colloids we can thus easily concentrate powerful activity on minute quantities (a few milligrams) of precipitated hydrosols. This method proves very convenient

\* See *e.g.* W. Biltz, *loc. cit.*

† Zsigmondy, *loc. cit.* p. 94.

when it is desired to concentrate radioactive products not only in the case of radium but equally well in the case of actinium, mesothorium, and uranium. The results of these researches, showing that in these cases too we have to deal with colloidal radioactive hydrosols, will be published elsewhere together with results obtained by the cataphoresis of the products. We may in the meantime point out, however, that the use of the methods described is subject to such restrictions as will allow of the colloidal state of the products being maintained.

#### 6. Capillary Analysis of Radioactive Products.

Investigating, as aforesaid, the dependence of the activity of a filter on the quantity of added colloid, I found that the filter manifested considerable activity, even when no foreign colloids were added. When water saturated with emanation together with its successive products was passed through a filter, a good part of the products (though not all) remained on it. I endeavoured to eliminate all possible impurities in the filter-paper, and for this reason I employed, after many trials, filters No. 590 (Schleicher & Schüll) having very little (0.03 mg.) ash remainder, previously extracted in hydrochloric and hydrofluoric acid. A filter so prepared showed again very strong activity.

One instance may be given here. 16 cm.<sup>3</sup> of water saturated with emanation were passed through the filter. After careful washing of the filter and desiccation by means of a Bunsen burner, it was introduced at once into the testing vessel, where its activity was measured. The results are shown below :—

TABLE I.

Time in minutes.	Activity.
2	254
6	278
10	318
15	355
28	387
40	323
103	174



It will be observed that the activity collected on the filter indicates the presence of RaB and RaC, and the corresponding curve of activity is identical with that shown by the cathode after electrolysis of pure water containing emanation. Hence it is natural to conclude that the deposits on the filter are positive hydrosols.

The well-known researches of Schönbein and Goppelsröder on the so-called capillary analysis were extended to the case of colloids by Fichter\* and Sahlboom†. The writers showed that various colloids do not ascend to equal heights in sheets of filter-paper: the negative colloids rise with the water, whereas the positive are precipitated in the immersed part of the sheet of paper; in a similar manner positive colloids are precipitated when filtered. Fichter and Sahlboom attribute the phenomena they observed to a negative electrization of the fibres of the paper taking place as the water passes through; this produces a neutralization and a consequent precipitation of the positive colloids.

The precipitation on the filter of the radioactive products which form positive hydrosols shows that in this case we have to do with the same phenomenon as that observed by Fichter and Sahlboom in the case of ordinary colloids. This inference was confirmed by further investigations. A small quantity of aluminium sulphate in solution was added to water containing emanation; the activity of the filter through which this water was passed is found to be greater than in the case when pure water with emanation was filtered; the curve of activity shows that in this case all the products (RaA, RaB, and RaC) remain on the filter. Now we know that under the influence of aluminium ions the negative hydrosols become inversely charged, and when electrolysis is going on are deposited at the cathode.

In like manner we may obtain a greater quantity of RaC and RaA on a filter by adding hydrochloric acid to the solution; this also produces a change of sign of negative hydrosols‡. The activities of filters through which acidulated solutions of emanation were passed changed in the same way as did the activities of the cathodes, when the solutions were electrolysed. In presence of acid in greater concentration RaB no longer appears at the filter, only RaA and RaC. In the case of a very strong concentration of the acid used (1 normal solution or more) the filter proved to be

\* Fichter, *Zeit. f. Kolloide*, viii. p. 1; *Verh. d. Naturfor. Ges. Basel*, xxi. p. 1.

† Sahlboom, *Kolloidchemische Beihefte*, ii. p. 79.

‡ Godlewski, *loc. cit.*

practically inactive. This last observation is of importance in so far as it clearly shows that the phenomenon with which we have to deal is due essentially to the precipitation of radioactive products in the colloidal state, and that it does not depend on a process of adsorption. At high concentrations of acid, indeed, we have no longer a colloidal, but rather an ionic solution, in which no precipitation occurs.

In the latter case, the products are prevented from being precipitated on the filter by being dissolved in a strong acid. We are able, however, to maintain the products in colloidal state without allowing them to remain on the filter. This may be done by transforming all radioactive products into negative colloids. If to a solution a sufficient amount (a few milligrams) of a negative colloid be added, *e. g.* of gold, platinum, or arsenious sulphide, the radioactive products pass freely through the filter, which shows no activity at all. The addition of 1 cm.<sup>3</sup> of  $\frac{1}{10}$  normal potassic citrate reduces similarly the activity of the filter to less than 10 per cent.; the effect of the citrate, as is known, is to change the sign of positive hydrosols, transforming them into negative ones; and the latter are not precipitated.

Experiments were also made to examine whether the precipitation of colloids which form the positive hydrosols could be shown by observing the ascent of water saturated with emanation in sheets of filter-paper. In the immersed part of the paper, RaB and RaC are found in the same relative amount as on the filters. When the sheets are immersed for a long time, we find also RaB and RaC in the parts lying above the surface of the liquid in its immediate proximity. At higher levels, however, only pure RaC was noticeable. The explanation of this is simple. Negative hydrosols only, *i. e.* RaA and RaC, can ascend in the paper. Of these, RaA can travel through a small distance only, because, owing to the short period of its transformation, it becomes soon transformed into RaB, which is precipitated. In consequence the RaC is the only one which ascends somewhat higher.

We can collect the radioactive products by filtration on glass-wool just as well as on paper.

The experiments so far described supply us with a new and strikingly simple method of concentrating radioactive products. For this purpose the products require only to be filtered. If, as frequently happens, they are to be collected on the smallest possible quantity of foreign substance, we have only to burn the filter, which reduces then to a negligible amount of ash. And since the process is based on a property belonging to all positive colloids in general, it follows that

the method will probably be applicable also to the concentration of products of thorium, actinium, and uranium. Some experiments I made with solutions of mesothorium and actinium have shown in fact that, by means of one filtration, certain products may be collected on the filter. The procedure may be further employed in the case of solutions of uranium products. One filtration of aqueous solution of uranium nitrate suffices to deprive uranium of the greater part of its  $\beta$  activity, which remains on the filter.

The method is convenient, not only because it is so very simple, but also because it will allow the activity (the products) to be concentrated on extremely small quantities of substance. It is applicable, however, in those cases only when radioactive products behave as positive colloidal hydro-sols in solution : to take an instance, in the case of uranium nitrate the solution must be very dilute (10 gr. of uranium salt per litre at most).

The results of experiments concerning the radioactive products of thorium, actinium, and uranium will be described in full in a subsequent paper.

Physical Laboratory of the Technical High School,  
Lemberg (Lwów).  
December, 1913.

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LXXI. *Light Absorption and Fluorescence.* By E. C. C. Baly, M.Sc., F.R.S., *Professor of Inorganic Chemistry in the University of Liverpool*\*.

IN two papers in conjunction with Miss E. G. Marsden† (Mrs. Solomon) and Mr. F. O. Rice‡, dealing with the relationship between absorption spectra and chemical reactivity, I have shown that it is possible for one substance to exhibit different absorption bands when dissolved in different solvents. If, for example, certain aromatic amino aldehydes and ketones are dissolved in alcohol, their solutions exhibit characteristic absorption bands in the ultra-violet region. If now to these alcoholic solutions a small quantity of an alcoholic solution of hydrogen chloride is added, the quantity being much less than is required to convert the whole of the amino compound into the hydrochloride, a second absorption band is developed of longer wave-length. On adding a further quantity of hydrogen chloride the absorption changes to that characteristic of the hydrochloride of the base. These

\* Communicated by the Author.

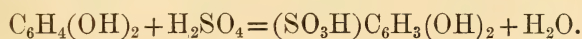
† Trans. Chem. Soc. xxiii. p. 2108 (1908).

‡ Ibid. ci. p. 1475 (1912).



observations lead to the inevitable conclusion that in the reaction by which the amino compound is converted into its hydrochloride, it passes through an intermediate phase which is formed in presence of small traces of the acid and, on the addition of more acid, reacts with this acid to give the salt. Here, therefore, we have evidence of the same substance exhibiting two different absorption bands in different solvents.

An exactly similar phenomenon was observed in the case of the sulphonation of certain benzene compounds. In the case of hydroquinone, for example, the chemistry of the process is represented by the equation



If hydroquinone is dissolved in alcohol the solution exhibits a very strong absorption band in the ultra-violet. A solution of hydroquinone in concentrated sulphuric acid, however, exhibits an absorption band which is much nearer to the red than that shown by the alcoholic solution. The acid solution on standing slowly changes to a solution of the sulphonic acid, and the change may be readily followed with the spectroscope. Clearly, therefore, the hydroquinone in the acid solution exists in an intermediate condition which proceeds to form the sulphonic acid. Clearly, also, the hydroquinone can show two absorption bands, one in alcoholic solution and the other in sulphuric acid solution.

In order to explain the shift of the emission spectrum lines of metals when the arc is formed under pressure, Humphreys\* postulated the existence of electromagnetic force fields surrounding each atom of the metal. This conception may be extended to the case of molecules. It would follow from the fact that the atoms of the different elements differ so much in their chemical characteristics that their electromagnetic force fields must also differ. In a molecule composed of several different atoms there will exist several electromagnetic force fields in close juxtaposition and differing amongst themselves. There must ensue, therefore, a condensing together of these force fields with the escape of energy and the formation of a closed force field having a materially reduced chemical reactivity. In fact the force field may be so closed that the reactivity becomes immeasurably small. In other cases a balance may be left over, giving rise to what chemists recognize as residual affinity. It follows from this view that in order to induce chemical reactivity it

\* *Astrophys. Journ.* xxiii. p. 233 (1906).



is necessary to open up the closed force field by some means. This may be done by solution in a solvent possessing free force lines or residual affinity, when the closed field of the solute is interpenetrated by the force lines of the solvent, and becomes unlocked and capable of reacting with another substance also in solution in the same solvent. In previous papers\* it has been pointed out how this conception is capable of giving an explanation of the phenomenon of stereoisomerism and catalysis.

The fact that more than one absorption band is given by one and the same substance in different solvents gives at once a reasonable explanation of phosphorescence and fluorescence. The various absorption bands exhibited by the same substance represent various free periods of vibration possessed by the same substance. If now a substance in alcoholic solution exhibits an absorption band and if it is absorbing light of this frequency, it is reasonable to expect that some of the vibrations corresponding to greater stages in the opening up of the closed force field are brought into play†.

If  $\lambda_1$  be the wave-length of the absorption band in alcohol when a substance has its force fields opened to a definite stage, and  $\lambda_2, \lambda_3$ , &c. be the wave-lengths of light absorbed when it is opened up to greater stages by solution in other solvents, then if the substance in alcoholic solution is absorbing light of wave-length  $\lambda_1$ , it is reasonable to expect that some of the more opened up phases will be called into play. In other words, the substance will fluoresce with emission of light of wave-length  $\lambda_2, \lambda_3$ , &c. The wave-length of the light absorbed by a substance when opened up to a greater stage by solution in a suitable solvent should therefore be the same as the fluorescent light emitted in alcoholic solution when it is only opened up to a lower stage. This has actually been found to be the case, for the fluorescent light emitted by a number of compounds in alcoholic solution is the same as that absorbed by them when in solution in sulphuric acid. Similarly the wave-length of the fluorescent light emitted by the alcoholic solutions of the amino aldehydes and ketones is the same as that absorbed by them in the presence of traces of hydrogen chloride‡.

It follows from this that the fluorescent spectrum of a compound will give a measure of a wave-length of the absorption band of that substance when opened up to a greater stage.

\* Baly, *Zeit. Elektrochem.* xvii. p. 211 (1911); *Phys. Zeit.* xiv. p. 893 (1913).

† Baly and Krulla, *Trans. Chem. Soc.* ci. p. 1469 (1912).

‡ Baly and Krulla, *loc. cit.*

Up to the present I have found only a few substances in which more than two absorption and fluorescent maxima have been measured; but in each of these there exists a constant frequency difference between these maxima. This is shown very clearly in the case of the substances given below.  $A_1$ ,  $A_2$  refer to absorption bands and F to fluorescent maxima. The measurements are expressed in terms of  $1/\lambda$ , and in order to convert them to oscillation frequencies they must be multiplied by  $3 \times 10^{11}$ .

	$A_1$ .	$A_2$ .	F.	Differences.	
				I.	II.
<i>o</i> -Aminocinnamic acid...	3600	2800	2000	800	800
$\beta$ -Naphthylamine .....	3600	3000	2400	600	600

A solution of benzaldehyde in strong sulphuric acid shows absorption bands at  $1/\lambda = 2174$  and 3400, the difference of frequency being 1226, which is twice 613. In alcoholic solution it shows two bands at  $1/\lambda$  3470 and 4070, the difference being 600. Clearly therefore the constant difference is shown here also. We should also expect to find an absorption band with a value of  $1/\lambda = 2787$ ; and it is interesting to note that the absorption curve of the sulphuric acid solution shows a "step out" in this region, which denotes that there is evidence of an absorption band about this position. The measurements of  $1/\lambda = 3400$  and 3470 evidently refer to the same band, the difference being due to the two solvents.

Similar constant frequency differences seem to be present in several other compounds, *e. g.* trinitroanisole and trinitrobenzene; but more accurate measurements are necessary before the fact of their existence can definitely be stated.

It is also interesting to note that a large number of compounds, for which only two maxima of absorption and fluorescence are known, show a frequency difference of 400 or some multiple of 400. The following examples may be given :—

	$A_1$ .	$A_2$ .	F.	Differences.
Phenol .....	3660	.....	3255	405
Dibenzylideneacetone .....	3200	2060	.....	$3 \times 380$
Dianisylideneacetone .....	2800	2000	.....	$2 \times 400$
Quinol dimethylether .....	3420	2210	.....	$3 \times 404$
Ethyl $\alpha$ -Benzoylsuccinate ...	4050	2800	.....	$3 \times 417$
$\alpha$ -Naphthol .....	3390	.....	2600	$2 \times 395$

These examples are sufficient to show not only that the constant frequency differences exist, but also that these differences are often  $1/\lambda = 400$  or some multiple of 400. It is not easy to measure the centre of an absorption band from an absorption curve as obtained with a spectrograph; and therefore great accuracy has not been possible in the above. Somewhat the same is true of fluorescent observations, for very little accurate work has been carried out on the position of the maximum. Investigations are now in progress in this laboratory both on absorption and fluorescence in order to determine whether this constant frequency difference is a general law. It is hoped that these results will shortly be ready for publication.

Now in any case of the selective absorption of light by a substance, it may be presumed that the light energy is absorbed in definite quanta, defined by the well-known expression  $h\nu$ , where  $h$  is the Planck constant and  $\nu$  the oscillation frequency of the absorption band. If now the absorption of the light energy is not accompanied by any photochemical change whereby new substances are produced, it is reasonable to make the simple assumption that the energy thus absorbed is transformed into heat and evolved again as such. Furthermore, if the substance possesses a characteristic absorption band in the infra-red, it is to be expected that the light energy absorbed will be evolved in radiation having the same wave-length as that of the infra-red absorption band. If this be the case, then this heat energy will also be evolved in quanta. The whole of the energy absorbed in the form of light should be evolved in the form of heat, and therefore for every quantum of light energy a certain number of complete quanta of heat energy must be evolved. If  $\nu_0$  be the oscillation frequency of the absorption band in the light region, and  $\nu_x$  be that of the band in the infra-red, then clearly

$$h\nu_0 = nh\nu_x \quad \text{and} \quad \nu_0 = n\nu_x,$$

where  $n$  is some whole number.

In words, the oscillation frequency of the ultra-violet absorption band should be a multiple of the oscillation frequency of the infra-red absorption band.

If the above assumption be justified, namely that a quantum of light energy absorbed is completely evolved as a whole number of quanta of light energy, and that the relation holds good that

$$n\nu_x = \nu_0,$$

then it is to be expected that there should also exist the various possibilities

$$(n-1)\nu_x = \nu_1,$$

$$(n-2)\nu_x = \nu_2,$$

$$(n-3)\nu_x = \nu_3,$$

&c.

That is to say, there should exist possibilities of the absorption by one and the same substance of light of frequencies  $\nu_1, \nu_2, \nu_3$ , &c., and that each quantum of energy  $h\nu_1, h\nu_2, h\nu_3$ , &c. thus absorbed should be evolved as  $h(n-1)\nu_x, h(n-2)\nu_x, h(n-3)\nu_x$ , &c. quanta of infra-red radiation respectively.

Since

$$\nu_0 - \nu_1 = \nu_1 - \nu_2 = \nu_2 - \nu_3 = \dots = \nu_x,$$

we should expect to find evidences of absorption bands with constant frequency differences exhibited by one and the same substance. Inasmuch as such constant frequency differences do exist between the absorption maxima, the deduction made from the energy quantum theory is experimentally verified.

Again, the absorption and fluorescent maxima appear to give a means of determining the values of  $\nu_1, \nu_2, \nu_3$ , &c. Since the differences  $\nu_1 - \nu_2, \nu_2 - \nu_3$ , &c. equal  $\nu_x$ , they should equal the frequency of a band in the infra-red. Presumably, however, this infra-red band should only be exhibited by the substance when in the opened up condition; and as yet no measurements have been made of infra-red absorption in this direction. This also I hope to be able to carry out in the near future.

It would seem that a further experimental verification might be sought in the refractivities of compounds which Sellmeyer has shown can be connected with an absorption band in the ultra-violet. Sellmeyer's formula in its simplest form is

$$\mu - 1 = \frac{N}{\nu_0^2 - \nu^2},$$

where  $N$  is a constant,  $\nu_0$  is the frequency of the ultra-violet absorption band, and  $\nu$  the frequency of the light for which a given value of the refractivity,  $\mu - 1$ , is found.

*Phil. Mag. S. 6. Vol. 27. No. 160. April 1914. 12 U*



The value of  $\nu_0$  is generally very large and lies in the extreme ultra-violet region beyond the working limit of a spectrograph in air. The value of  $\nu_0$  is therefore calculated from the refractivities for two different values of  $\nu$ . Now if each energy quantum  $h\nu_0$  absorbed is evolved as a whole number of quanta of infra-red radiation, it is obvious that we can replace  $\nu_0$  in the formula by some multiple of the frequency of the infra-red absorption band. In doing this it must be remembered that we are not dealing with substances which have their closed force fields opened up by solvents or in any other way. The infra-red absorption bands have been observed with considerable accuracy in the case of many substances, and recently Mr. and Mrs. Cuthbertson\* have published the refractivities of several gases for which the wave-lengths of the infra-red absorption bands are known fairly accurately. Calling the frequency of the infra-red band  $\nu_y$ , the value  $n\nu_y$ , where  $n$  is a whole number, can be substituted in Sellmeyer's formula, so that it reads

$$\mu - 1 = \frac{N}{(n\nu_y)^2 - \nu^2}.$$

This should give a very accurate means of calculating the refractivities. I have done this for the following substances given by Mr. and Mrs. Cuthbertson: chlorine, hydrogen chloride, water vapour, ammonia, nitric oxide, and nitrous oxide; and the results of the calculation are given in the following tables.

The method of calculation is very simple, for it is only necessary to find which multiple of  $\nu_y$  gives the best values of the constant  $N$  in the formula, making use of the observed values of the refractivities. The mean value of the constant  $N$  is then found and inserted in the formula, and the refractivities calculated. The following values were obtained:—

#### *Water Vapour.*

$\lambda$  (infra-red bands) =  $2.95 \mu$  †, whence  $\nu_y = 1.017 \times 10^{14}$ .

The following are the refractivities calculated from the

\* C. Cuthbertson and M. Cuthbertson, Phil. Trans. ccxiii. A. p. 1 (1913).

† Coblentz, Carnegie Institution Publications No. 35, p. 56 (1905).

formula

$$\begin{aligned}\mu-1 &= \frac{2.6002 \times 10^{27}}{(32 \times 1.017 \times 10^{14})^2 - \nu^2} \\ &= \frac{2.6002 \times 10^{27}}{10590 \times 10^{27} - \nu^2}.\end{aligned}$$

Values of  $(\mu-1)10^8$ .

$\lambda$ .	Calculated.	Observed.	Differences.
6708	25026	25028	-2
6438	25068	25069	-1
5790	25192	25191	+1
5770	25195	25195	0
5461	25274	25270	+4
5209	25347	25345	+2
5086	25387	25380	+7
4800	25494	25495	-1

In order to show how accurately the results appear if the correct multiple of  $\nu_y$  be used, I have calculated out the refractivities of water vapour using the factors 31 and 33 instead of 32 as above. The values in the two following tables are obtained with the formulæ

$$\mu-1 = \frac{2.4356 \times 10^{27}}{9938.5 \times 10^{27} - \nu^2}, \text{ where } 9938.5 \times 10^{27} = (31\nu_y)^2,$$

and

$$\mu-1 = \frac{2.7703 \times 10^{27}}{11262 \times 10^{27} - \nu^2}, \text{ where } 11262 \times 10^{27} = (33\nu_y)^2.$$

Values of  $(\mu-1)10^8$   
when  $n=31$ .

Values of  $(\mu-1)10^8$   
when  $n=33$ .

$\lambda$ .	Calc.	Obs.	Diff.	$\lambda$ .	Calc.	Obs.	Diff.
6708	25010	25028	-18	6708	25038	25028	+10
6438	25054	25069	-15	6438	25077	25069	+8
5790	25187	25191	-4	5790	25194	25191	+3
5770	25192	25195	-3	5770	25198	25195	+3
5461	25274	25270	+4	5461	25271	25270	+1
5209	25352	25345	+7	5209	25340	25345	-5
5086	25396	25380	+16	5086	25378	25380	-2
4800	25509	25495	+14	4800	25480	25495	-15

The progressive change in the errors column is manifest.

*Hydrogen Chloride.*

$\lambda$  (mean of the two infra-red hands) =  $3.474 \mu^*$ , whence

$$\nu_y = 8.636 \times 10^{13}.$$

In this case the value of  $\frac{\nu_0}{\nu_y} = 38$ , and the following formula was used:

$$\mu - 1 = \frac{4.6896 \times 10^{27}}{10769 \times 10^{27} - \nu_y^2}, \text{ where } 10769 \times 10^{27} = (38\nu_y)^2.$$

Values of  $(\mu - 1)10^8$ .

$\lambda$ .	Calculated.	Observed.	Differences.
6708	44372	44375	-3
6433	44444	44444	0
5790	44656	44656	0
5770	44669	44666	+3
5461	44803	44800	+3
5209	44930	44930	0
5086	45001	45007	-6
4800	45187	45187	0

The paper by Fraulein von Bahr has only just been published, and the values given above are far better than those calculated with the measurement of the absorption band of hydrogen chloride  $3.41 \mu$ , given by Ångström and Palmaer. The value  $3.474$  is clearly more accurate, and it is extremely satisfactory to find that the refractivities calculated from it agree more closely with the observed values. It is very possible that a re-determination of the absorption band of chlorine would improve the agreement between the calculated and observed refractivities shown in the ensuing table.

*Chlorine.*

$\lambda$  (infra-red band) =  $4.28 \mu \dagger$ , whence  $\nu_y = 0.70094 \times 10^{14}$ .

In this case the value of  $\frac{\nu_0}{\nu_y} = 44$ , and therefore the following formula was used:

$$\mu - 1 = \frac{7.224 \times 10^{27}}{9511.8 \times 10^{27} - \nu_y^2}, \text{ where } 9511.8 \times 10^{27} = (44\nu_y)^2.$$

\* Eva v. Bahr, *Deutsch. phys. Gesell. Verh.* xv. p. 1150 (1913).

† Ångström and Palmaer, *Öfvers. K. Vet.-Ak. Handl.* 1893, No. 6.

Values of  $(\mu-1)10^8$ .

$\lambda$ .	Calculated.	Observed.	Differences.
6708	77548	77563	-15
6438	77691	77703	-12
5709	78121	78121	0
5770	78137	78135	+2
5461	78406	78400	+6
5209	78659	78651	+8
5086	78798	78791	+7
4800	79166	79166	0

*Ammonia.*

$\lambda$  (infra-red band) =  $2.95 \mu^*$ , whence  $\nu_y = 1.01695 \times 10^{14}$ .

In this case the value of  $\frac{\nu_0}{\nu_y} = 28$ , and therefore the following formula was used :

$$\mu - 1 = \frac{2.9555 \times 10^{27}}{8108.1 \times 10^{27} - \nu^2}, \text{ where } 8108.1 \times 10^{27} = (28\nu_y)^2.$$

Values of  $(\mu-1)10^8$ .

$\lambda$ .	Calculated.	Observed.	Differences.
6708	37373	37376	-3
6438	37458	37455	+3
5790	37700	37701	-1
5770	37707	37707	0
5461	37857	37860	-3
5209	38006	38002	+4
5086	38086	38083	+3
4800	38296	38300	-4

*Nitric Oxide.*

$\lambda$  (mean of the two closely situated infra-red bands) =  $5.33 \mu^\dagger$ , whence  $\nu_y = 0.56235 \times 10^{14}$ . In this case the value of  $\frac{\nu_0}{\nu_y} = 62$ , and the following formula was used:

$$\mu - 1 = \frac{3.5261 \times 10^{27}}{12233.8 \times 10^{27} - \nu^2}, \text{ where } 12233.8 \times 10^{27} = (62\nu_y)^2.$$

\* Coblentz, Carnegie Institution Publications No. 35, p. 53 (1905).

† Warburg and Leithauser, *Ann. der Physik*, xxviii. p. 313 (1909).



Values of  $(\mu-1)10^8$ .

$\lambda$ .	Calculated.	Observed.	Differences.
6708	29302	29306	-4
6438	29346	29344	+2
5790	29470	29468	+2
5770	29474	29474	0
5461	29550	29550	0
5209	29626	29622	+4
5086	29667	29666	+1
4800	29774	29776	-2

*Nitrous Oxide.*

$\lambda$  (infra-red band) =  $4.47 \mu^*$ , whence  $\nu_y = 0.67114 \times 10^{14}$ .

In this case the value of  $\frac{\nu_0}{\nu_y} = 50$ , and the following formula was used :

$$\mu - 1 = \frac{5.5896 \times 10^{27}}{11261 \times 10^{27} - \nu^2}, \text{ where } 11261 \times 10^{27} = (50\nu_y)^2.$$

Values of  $(\mu-1)10^8$ .

$\lambda$ .	Calculated.	Observed.	Differences.
6708	50534	50544	-10
6438	50614	50616	-2
5790	50848	50848	0
5770	50857	50857	0
5461	51002	51000	+2
5209	51143	51145	-2
5086	51216	51208	+8
4800	51419	51415	+4

The agreement between the calculated values of the refractivities and those actually measured by Mr. and Mrs. Cuthbertson is exceedingly close in all the above six substances. The agreement is indeed as good as Mr. and Mrs. Cuthbertson themselves obtained using Sellmeyer's formula, the constants of which they calculated from their observed refractivities in each case by the method of least squares. The oscillation frequencies thus found for the ultra-violet absorption bands are therefore only theoretical, as they have not actually been observed and measured. The values given in the tables above have the materially important advantage that they have been calculated from an absorption band that has been measured.

\* Warburg and Leithausser, *loc. cit.*

The existence of absorption bands and fluorescence maxima with constant frequency differences, and the results of the above calculations, seem to show fairly conclusively that the application of the quantum theory to absorption spectra observations is thoroughly justified. Many interesting deductions may be made from this application. Thus, since it would seem that phosphorescence and fluorescence only differ in the relative velocity and absorption of the energy, and since the emission of infra-red radiation appears to be intimately connected with absorption in the ultra-violet, it is to be expected that the converse would be true. This may indeed give an explanation of the well-known fact that the phosphorescence of a substance after exposure to an exciting cause is at once destroyed on exposure to infra-red radiation.

Finally, since refractivity and magnetic rotation are bound up with chemical structure, it should be found possible on the above grounds to connect these properties with absorption and constitution more intimately than has hitherto been found possible.

Inorganic Chemistry Laboratory,  
The University, Liverpool.

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LXXII. *The Slip-Curves of an Amsler Planimeter.*

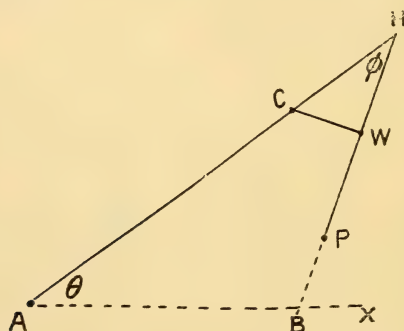
By A. O. ALLEN, M.A.\*

IT was shown by Lang in the *Allgemeine Vermessungs-Nachrichten* for 1894, in an article on the Amsler Planimeter, that when the pivot of the instrument has been fixed on the paper, a family of curves may be drawn round it having the property that while the tracing-point moves along any one of them the reading of the wheel is constant, since it slips without rolling. The importance of these curves is that the instrument works least accurately when the tracer travels nearly along any of them; consequently, in measuring an area the pole should be so chosen that at all points of the perimeter the tracer may as far as possible cut the slip-curves orthogonally. It is sometimes advisable to divide the area into portions and use a different pole for each portion so as to attain this end. Lang recommends that a template should be cut out in stiff paper, having the form of one of the slip-curves as found empirically; by revolving this about the pole as centre it is then easy to see which portions of the perimeter are inconveniently situated (Henrici, B. A. Report, 1894).

\* Communicated by the Author.

It will, however, be found that certain portions of the curves are not at all easy to draw empirically, and it seems preferable to draw the curve from its equation, which is deduced below.

A knowledge of the chief (and easily obvious) geometrical properties of the curve leads to a proof of the principle of Amsler's Planimeter, differing from all those which are to be found in the usual text-books, and superior to them (in my opinion) in the way in which it combines simplicity with true insight into the geometrical notions underlying the use of the instrument. A knowledge of the equation is not at all necessary for this purpose. Let AHP represent the essential parts of the planimeter, A being the pole, H the hinge, P the tracing-point, and W the point of contact of the recording wheel; then it is required to find the locus of P such that the point W shall always move in the direction of the line PH. Or to state the same thing in another way, we require the locus of P revolving about the instantaneous centre C, CW being perpendicular to PH.



Let AX be the initial position of AH; put  $\theta, \phi$  for the angles XAH, AHP respectively; also  $AH = a$ ,  $HW = c$ ,  $HP = b$ ,  $AP = r$ . Let the point P reach a consecutive point on the slip-curve by two distinct motions; first let the whole instrument move as if rigid through an angle  $d\theta$  about A, so that W moves off the line PH a perpendicular distance  $(a \cos \phi - c)d\theta$ . Next bring it back on to the line PH by a rotation  $d\phi$  of the arm HP, AH remaining fixed; hence  $c d\phi = (a \cos \phi - c)d\theta$ , which is the simplest equation of the slip-curve. Put  $\frac{c}{a} = \cos \alpha$ , so that  $\alpha$  is the value of  $\phi$  when P is on the slip-circle referred to below; integration then gives

$$\theta = \frac{c}{\sqrt{a^2 - c^2}} \left( \log \sin \frac{\phi + \alpha}{2} - \log \sin \frac{\phi - \alpha}{2} \right).$$

Taking AB as  $x$ -axis, the coordinates of P are

$$x = a \cos \theta - b \cos (\theta + \phi), \quad y = a \sin \theta - b \sin (\theta + \phi),$$

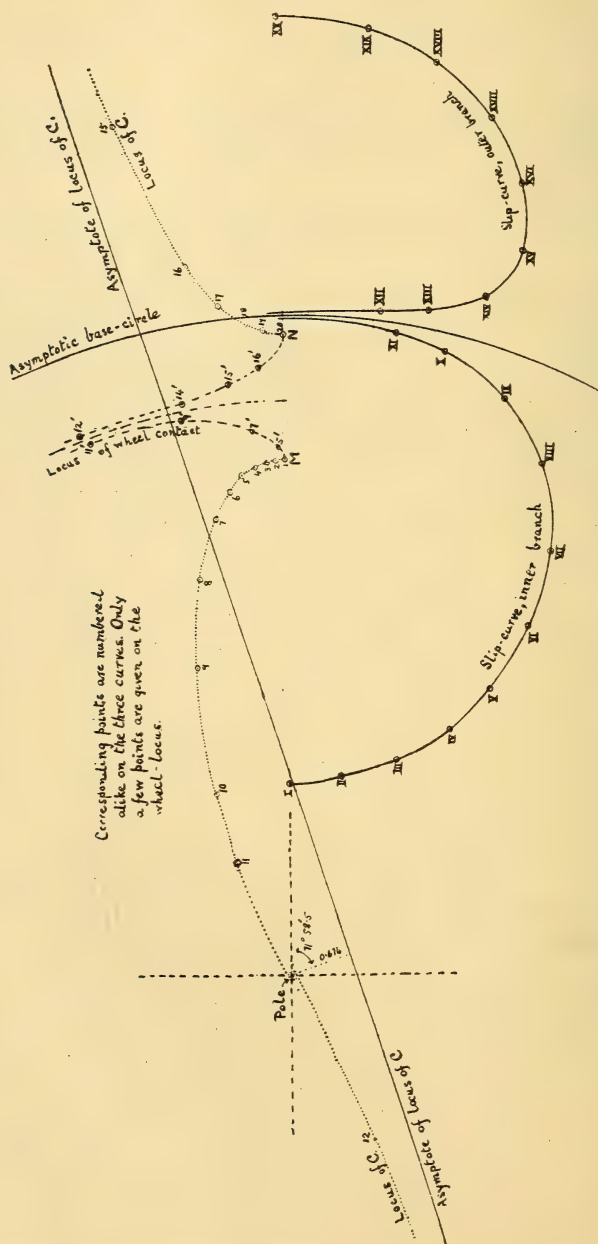
from which the curve may easily be drawn by assigning values to  $\phi$  between the limits 0 and  $\pi$ . If  $\theta$  is required in degrees, and if tabular logarithms of sines are used, the equation is

$$\theta = \frac{180}{\pi} \cdot \frac{c \log_e 10}{\sqrt{a^2 - c^2}} \left( L \sin \frac{\phi + \alpha}{2} - L \sin \frac{\phi - \alpha}{2} \right).$$

The diagram accompanying this paper shows one of the curves for a planimeter in which  $a = 6.305$  in.,  $b = 4.225$ ,  $c = 0.674$ ,  $\alpha = 83^\circ 52'$ . The points are denoted by Roman numerals, the successive values selected for  $\phi$  being  $0^\circ 0'$ ,  $7^\circ 57'$ ,  $17^\circ 23'$ ,  $27^\circ 15'$ ,  $35^\circ 54'$ ,  $46^\circ 51'$ ,  $57^\circ 44'$ ,  $68^\circ 55'$ ,  $76^\circ 12'$ ,  $80^\circ 42'$ ,  $82^\circ 14'$ ,  $85^\circ 21'$ ,  $86^\circ 56'$ ,  $91^\circ 49'$ ,  $102^\circ 14'$ ,  $116^\circ 3'$ ,  $130^\circ 25'$ ,  $146^\circ 27'$ ,  $161^\circ 36'$ ,  $180^\circ 0'$ . These have merely been chosen so as to give convenient points on the locus. When  $\phi = 83^\circ 52'$ ,  $\theta$  is infinite, and  $x$  and  $y$  are indeterminate, giving any point whatever on the slip-circle or so-called "base-circle." Its radius is  $\sqrt{a^2 - c^2}$ , i. e. 7.20 in., and it obviously has the property that if the tracer be taken round it, the wheel will only slip, since  $\phi$  will be constant and AW will be always normal to PH. The slip-curves are a family of similar curves, each of which approaches the base-circle asymptotically from within and without; it will be noticed that the approach is very rapid, being almost complete before a single convolution about the pole has been described.

The diagram also shows the corresponding points on the locus of W (Arabic numerals, primed) and on the locus of C (Arabic numerals). There is no practical value attaching to the latter, but from the geometric standpoint it is interesting. It consists of two long flat branches; the first starts from the point M ( $a - c$ , 0) at right angles to the  $x$ -axis, approaches the pole O and performs an infinite number of convolutions about it in the anti-clockwise direction; it then performs convolutions in the opposite sense and goes to  $-\infty$  along the asymptote. The other branch returns from  $+\infty$  along the asymptote, on the opposite side of it, and finally runs into the point N ( $a + c$ , 0) at right angles to the  $x$ -axis. The correspondence between various portions of this curve and those of the slip-curve are interesting; the inflexion on the outer branch of the slip-curve of course corresponds to the points at infinity on the C-locus, while





the base-circle corresponds to the infinitesimal convolutions round the pole. The line joining corresponding points on the two curves is of course normal to the slip-curve. The equation to the locus of W only differs from that of P in having  $c$  instead of  $b$ . The locus of C is easily found; the vectorial angle of any point is the  $\theta$  given above; the radius vector is  $a - c \sec \phi$ , and on eliminating  $\phi$  we obtain

$$r \left( a \pm c \cosh \frac{\theta \sqrt{a^2 - c^2}}{c} \right) = a^2 - c^2.$$

The asymptote is  $r \sin (\beta - \theta) = c$ , where

$$\beta \tan \alpha = \log_e \cot \left( \frac{\pi}{4} - \frac{\alpha}{2} \right);$$

in this diagram  $\beta = 18^\circ 1'5$ .

With a general knowledge of the character of the slip-curves we can easily establish the validity of the method by which the instrument substitutes a line-integral for a surface-integral, as follows.

Consider first an area PQRS bounded by two circular arcs PQ and RS with the pole as centre, and by portions of two slip-curves QR, PS; and let PQ, RS each subtend an angle  $\epsilon$  at the pole. Then while PQ is traced there is no change in the angle at H; the wheel moves over a circular arc of length  $\epsilon \cdot AW$ , but only records

the component  $\epsilon \cdot AW \cdot \cos AWP$ , i.e.  $\epsilon (AH \cos \phi_1 - HW)$  or  $\epsilon (a \cos \phi_1 - c)$ , where  $\phi_1$  is the angle at H during this part of the cycle. From Q to R nothing is recorded, but the angle at H alters to  $\phi_2$ ; from R to S the record is  $-\epsilon (a \cos \phi_2 - c)$ ; from S to P nothing is added. The whole record is  $a\epsilon (\cos \phi_1 - \cos \phi_2)$ . If the radii of the arcs PQ, RS are  $r_1, r_2$ , this is the same as

$$a\epsilon \left( \frac{r_2^2 - r_1^2}{2ab} \right), \quad \text{i.e.} \quad \frac{\epsilon}{2b} (r_2^2 - r_1^2).$$

But the area is

$$\int_{r_1}^{r_2} \epsilon r dr, \quad \text{i.e.} \quad \frac{\epsilon}{2} (r_2^2 - r_1^2),$$

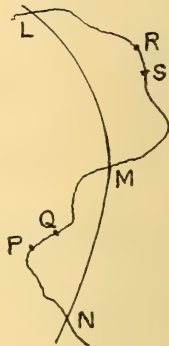
so that the area is  $b$  times the line-integral recorded.

Hence the area is  $2\pi Rb$  for each revolution of the wheel,  $R$  being the radius of the wheel; it is generally so chosen that  $2\pi Rb = 10$  sq. ins., *e. g.* in this case the diameter of the wheel is almost exactly  $\frac{3}{4}$  of an inch.

It has been tacitly assumed that  $P$  and  $S$  lie on the same branch of the slip-curve; if they are separated by the base-circle, a different expression of the facts may be adopted. The journey from  $P$  to  $Q$ , then out on to the base-circle by a slip-curve and back along another slip-curve to  $P$ , will record simply  $(a \cos \phi_1 - c)\epsilon$ . Then from  $P$  back along the slip-curve on to the base-circle, so along the slip-curve to  $R$ , then to  $S$ , and finally back by a slip-curve, the record will be  $-(a \cos \phi_2 - c)\epsilon$ , and this will be added to the previous one. The only difference from the last case is that the numerical value of this second term is now positive, whereas it was negative before.

It is easy now to see how an area of any shape may be split up into elements of this kind and the proof then generalized.

A possibility not yet considered is that the pole may lie within the area to be measured (but of course at not more than  $a+b$  nor less than  $a-b$  from any point of the perimeter). In this case let  $LMN$  be part of the base-circle,  $LRSM$  and  $MQPN$  being portions of the perimeter respectively external and internal to this circle. Then the record during the journey  $LRSM$  evidently gives the area of the figure  $LRSM$ , positively; during the journey along  $MPQN$  we are travelling along the perimeter *in the same sense*, but inside the base-circle instead of outside, so that the wheel will be rotating in the opposite sense, and we shall therefore have the area  $MQPN$  recorded negatively. Proceeding thus all round the perimeter, it is clear that what is recorded is merely the *excess* of the area of the curve above that of the base-circle; it is therefore necessary to add the latter, viz.  $\pi(a^2 + b^2 - c^2)$ . This area is generally engraved on the weight which keeps the foot of the instrument pressed into the paper; in the present instance it is 179.54 sq. ins.



LXXIII. *The Electrical Resistance of Nickel in Magnetic Fields.* By W. MORRIS JONES, B.Sc., and J. E. MALAM\*.

THE influence of magnetic fields on metallic resistance has been studied by numerous investigators. The two main cases observed have been those in which the magnetic field is respectively parallel and perpendicular to the direction of the current in the metal. The longitudinal effect for nickel and iron has been investigated for small magnetic fields by Williams†. Barlow‡, Patterson§, Owen||, and Heaps¶ have used an electromagnet and obtained results for large magnetizing forces. The transverse effect for different metals has been carefully studied by Grunmach\*\*. More recently, Knott†† has obtained novel results for nickel by combining small longitudinal and transverse fields.

Owen, using wires about 1 mm. long, investigated the longitudinal effect for nickel up to fields of 30,000 c.g.s. units. He found that the change of resistance attained a maximum at a field of 2800 c.g.s., decreasing to a constant minimum reached in a field of about 24,000 c.g.s.

Heaps, using a fine wire mounted in zigzag fashion on a strip of mica, studied the same effect for fields up to 10,000 c.g.s. units. He concluded that the increase of resistance approached a maximum but did not grow less after reaching the maximum. The slight decrease actually obtained (about  $\frac{1}{11}$  of the maximum increase at a field of 10,000 c.g.s.) he attributed to non-uniformity of the field and to the slight transverse field introduced by bending back the wire upon itself. The drop obtained by Owen (in one case at a field of 10,000 c.g.s. about  $\frac{1}{10}$  of the maximum increase) Heaps attributed to the difficulty of setting such small wires accurately parallel to the field. He further suggested that for very short wires the polarity of the metal might have some effect in disturbing the field.

The investigations described below were undertaken with the object of throwing some light on the discrepancy between the results for the longitudinal effect in nickel obtained by Heaps and Owen. As the experiments proceeded their scope was somewhat widened, the transverse effect and the effects for intermediate orientations being included.

An important feature of the experimental arrangements

\* Communicated by Prof. E. Taylor Jones.

† Phil. Mag. vi. p. 693 (1903); ix. p. 77 (1905).

‡ Proc. Roy. Soc. lxxi. p. 30 (1902).

§ Phil. Mag. iii. p. 643 (1902).

|| Phil. Mag. xxi. p. 122 (1911).

¶ Phil. Mag. xxii. p. 900 (1911).

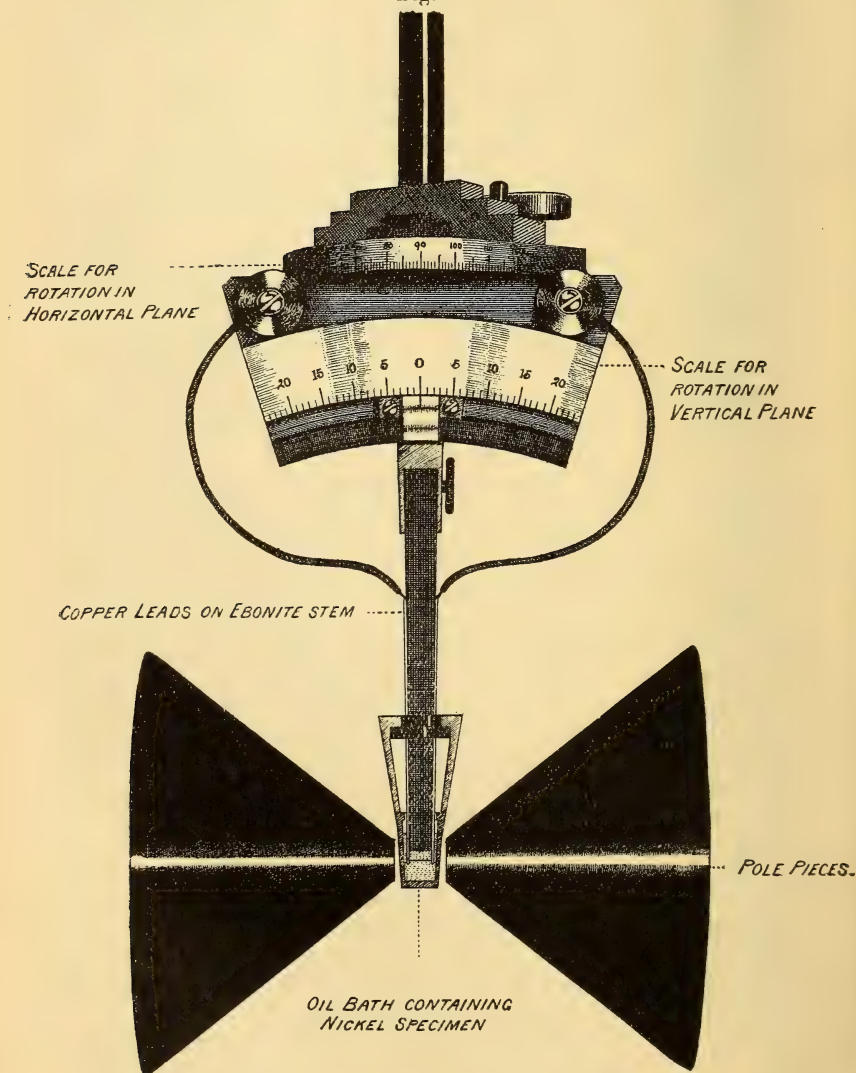
\*\* *Annalen der Physik*, xxii. p. 141 (1907).

†† Proc. Roy. Soc. Edin. xxxiii. pt. 2, no. 20 (1913).



650 Messrs. W. Morris Jones and J. E. Malam on the  
 was the instrument shown in fig. 1. By means of this  
 arrangement the difficulty of accurate setting is obviated.

Fig. 1



The instrument is so constructed that when once the necessary adjustments have been accurately made the middle point of the specimen will remain at the common vertex of the conical pole-pieces during any rotation. The specimen, in the form of a fine wire of length  $\cdot 361$  cm. and

diameter .00206 cm., was passed through fine holes at the ends of copper leads attached to an ebonite stem of square cross-section. The solder was applied to the outer sides of the leads, and finally carefully filed down in order to remove any end portions of the specimen which might not be longitudinal. Great care was exercised during this operation and the whole finally examined under a microscope in order to ensure that the wire was perfectly straight. Flexible wires soldered to the ends of the copper leads were twisted together as far as possible and connected to the terminals shown. In the figure they are separated for the sake of clearness. Terminals at the back of the instrument served to connect up the specimen to a thick twisted cable suspended by silk cords from the beams of the laboratory and leading to one of the gaps of a slide-wire bridge 30 feet from the electromagnet. The whole instrument was carried by a metal carriage sliding on a rigid framework above the poles of the magnet in such a manner that the specimen could be brought out of the field in a direction perpendicular to the axis of the pole-pieces. The whole arrangement was made as rigid as possible, to ensure the return of the specimen to exactly the same place in the field. By means of screws provided on the instrument the specimen could be rotated in either a horizontal or a vertical plane, the amount of rotation being measured on the scales shown in the figure. An ebonite oil-bath with mica sides was sprung on to a circular collar fixed to the stem, and could be kept in position between the pole-pieces when the specimen was rotated in a horizontal plane. It was thus possible, while investigating the effects for various orientations, to place the pole-pieces much nearer together than could be done with an oil-bath fixed rigidly to the stem.

The instrument was first adjusted by means of nuts attached to the sliding carriage until the specimen was as nearly as possible at the right height between the pole-pieces, a travelling microscope being employed for the purpose. Any small inclination of the wire to the common axis of the cones was corrected by slightly rotating the lower portion of the instrument. A final adjustment was made by altering the position of the brass stop used in connexion with the sliding carriage, in order that the specimen should be stopped as accurately as possible at the right position in the field, an inclined mirror placed under the pole-pieces being used during this operation.

The changes of resistance were measured by means of a slide-wire bridge similar to that described by Owen (*Phil. Mag.* xxi. p. 122, 1911). The sensitiveness of the arrangement was, however, largely increased, the maximum step

employed varying from 40 to 75 cm., as against 18 cm. used by Owen. Auxiliary coils of german-silver wire were immersed in the same ebonite oil-bath and placed in two gaps of the bridge, the specimen and a standard ohm used as a comparison resistance being placed in the other two gaps respectively. The riders sliding on the bridge-wire were fastened to continuous strings passing round pulleys placed near the ends of the bridge-wire and also on a table about 8 ft. from the bridge, at which the person measuring the changes of resistance sat. The experimenter could thus operate the riders while observing the galvanometer with a telescope and scale. It was found that quick and delicate adjustment could be obtained by this method, the arrangement allowing of very minute movements of the riders, to which the galvanometer readily responded. The mercury key used in changing riders could also be operated from a distance. All resistances were placed in pure paraffin insulating oil and little trouble was experienced from temperature variation. When a series of observations for a curve was taken with steadily increasing fields it was found that the balancing point on the bridge for zero field invariably rose steadily through a small range (about  $\frac{1}{2}$  of the total step for the longitudinal position) during the taking of the curve, owing partly to progressive heating of the specimen, and to a small extent to hysteresis. This variation has a very small effect on the percentage increase of resistance, the maximum correction calculated for temperature variation being about  $\frac{1}{300}$  of the maximum step. Any differences between curves taken with fields increasing or decreasing in regular sequence and those taken with high and low fields alternately or following each other in any irregular manner, were found to be within the limits of experimental error. The platinoid compensating coil and the water-cooling apparatus used by Owen in connexion with the electromagnet were discarded. It was found that after balancing for a field of 15,000 c.g.s. the current in the magnet (about 20 amperes) could be left running for five minutes without producing any appreciable change in the zero point on the bridge, the maximum galvanometer creep observed corresponding to about  $\frac{3}{1000}$  of the maximum step, whereas balancing could be accomplished in much under half a minute. On the other hand, if the magnet is water-cooled it is difficult to secure that the temperatures in the gap between the pole-pieces and at the place outside the pole-pieces where the specimen is put for balancing in zero field shall be exactly the same, and unsteadiness of the balancing point arises for this reason.



The electromagnet produced fields up to 15,000 c.g.s. units with pole-faces 8 mm. in diameter and .98 cm. apart. The semivertical angle of the conical pole-pieces was approximately  $39^\circ$ .

A sensitive Broca galvanometer the combined resistance of whose coils was 90 ohms was used, and worked very satisfactorily.

In taking readings, the balancing point on the bridge was first obtained with the specimen in zero field. The specimen was then slid in between the pole-pieces. The magnet current was turned on and the new balancing point obtained with a second rider. The difference of readings gave the step on the bridge. Demagnetization was effected by means of a reversing key operated automatically by the movement of one of the plates of a liquid-resistance box, which slowly diminished the current at the same time. Good demagnetization was obtained by this method. The specimen was then slid from between the pole-pieces of the magnet and balance again obtained with the specimen in zero field, the cycle of operations being repeated.

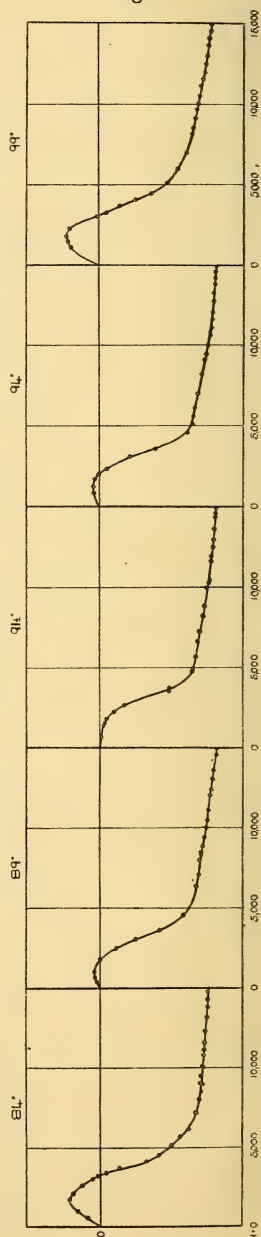
Field strengths were measured by the ballistic method, using an exploring coil 5 mm. in diameter.

In determining the accurate orientation of the specimen with regard to the external field the method of procedure was as follows. The pointer in connexion with the vertical scale was kept at the zero (or the corrected zero). The specimen could then be rotated in the horizontal plane containing the common axis of the pole-pieces by turning the screw connected with the pointer for the horizontal scale. This pointer was placed at say the division marked  $110^\circ$ , for which position the specimen may or may not be accurately at an angle of  $110^\circ$  with the longitudinal field. A series of observations was taken, the results being plotted in a curve. The pointer for the horizontal scale was then rotated through a few degrees towards the transverse position and another curve taken. This process was repeated until a series of curves for short intervals on each side of the transverse position had been obtained. Assuming the curves symmetrical for equal intervals on each side of the transverse position (a result justified by the fact that reversal of the field has no effect on the magnitude of the change of resistance), the comparison of similar curves furnishes a guide for further experiments at intermediate intervals. In this manner we can finally arrive at a series symmetrical for equal intervals on each side of the transverse position, and thus determine the true transverse position very exactly.



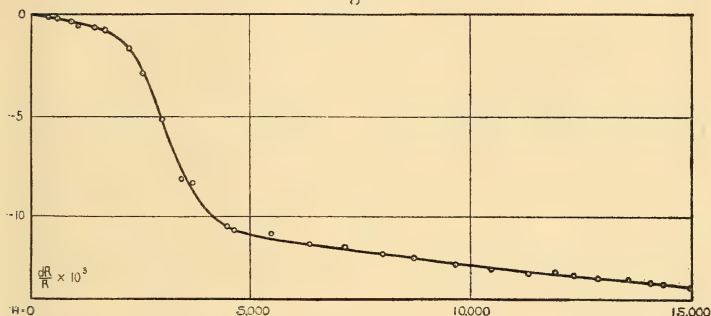
Such a series is reproduced in fig. 2, and it will be seen that the agreement between corresponding curves is good. The figures at the head of each curve give the respective scale-readings. It will be seen that the outer curves indicate  $91\frac{1}{2}^\circ$  on the scale as the true transverse position. The curve for this position is plotted on a larger scale in fig. 3. For fields below 1000 c.g.s. galvanometer deflexions were observed and the galvanometer afterwards calibrated. It will be seen that the values obtained for the changes of resistance are wholly negative. This result differs from that of Grunmach and Heaps, who obtained a few positive values for fields below 1000 c.g.s. units. The series of curves, however, furnishes the interesting evidence that if an error of setting of  $2\frac{1}{2}^\circ$  or even less is made with the transverse position as determined electrically, we shall obtain the result of Grunmach and Heaps. It is probable that an adjustment appearing mechanically correct may easily differ by this small amount from the true magnetic position, especially when comparatively short lengths of wire are employed. If when in a small transverse field of say 400 c.g.s. the specimen was rotated out of position through  $1^\circ$ , it was found that the galvanometer deflexion changed from negative to positive. A series of graphs of galvanometer deflexions for small fields for positions at intervals of  $1^\circ$  about the transverse position further supported the conclusion that a very small error of setting would account for the slight rise obtained by the above mentioned experimenters. It may be noted that in recent experiments

Fig. 2.



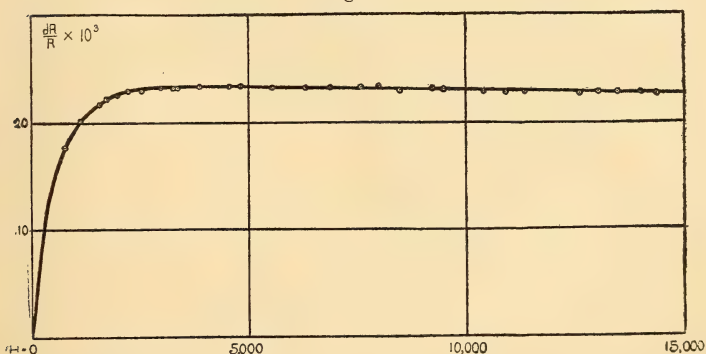
with a nickel strip Knott observed no increase of resistance in the lower transverse fields. He attributes the discrepancy between his results and those of Grunmach and Heaps to the difference in width in the direction of the magnetizing force.

Fig. 3.



Having obtained the transverse position, a similar series of curves was taken for the longitudinal position. As was to be expected, the curve with the least fall was obtained for the position  $1\frac{1}{2}^\circ$ . This curve is given in fig. 4. Curves

Fig. 4.



were taken for rotations of  $1^\circ$  about this position both in a vertical and in a horizontal plane. No curve with less fall was obtained after repeated experiment with different specimens. It will be noted that the change of resistance attains a maximum in a field of about 3000 c.g.s. The fall at 10,000, reckoned as a fraction of the maximum increase, is about  $\frac{1}{66}$ . As far as can be judged from the published curves, Heaps' fall at 10,000 is about  $\frac{1}{41}$ . This result thus affords a confirmation of that obtained by Heaps, the fall at 10,000 being slightly less than that obtained by him. This

is to be expected in view of the fact that Heaps' wire was bent back on itself several times, thus introducing a slight transverse component. It seems probable that, as Heaps suggested, the slight fall obtained is mainly due to non-uniformity of field. The correction for polarity is small. The length of the specimen was roughly 175 diameters, giving a self-demagnetizing factor of less than .02. Taking the saturation value of intensity of magnetization for nickel (hard-drawn) as 400, the true mean value of the external field will be less than that of the undisturbed field by roughly 8 c.g.s. units for fields above say 2000 c.g.s. (below which value saturation is obtained) with the specimen in the longitudinal position. This small constant correction would not account for the steady fall in the curve. It is also evident from the above that any small transverse disturbance introduced by the polarity of the metal would, with the specimen in the longitudinal position, be of such magnitude as to be negligible.

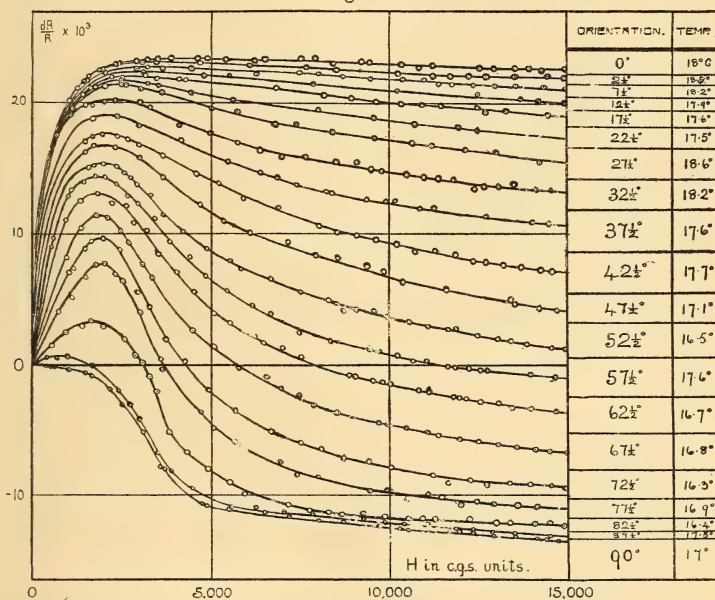
The specimen was soldered to the leads under a tension of about 6 kilogrammes per square cm. Owing to this initial stress the change of resistance for high fields would be slightly diminished. The magnitude of the effect of the changes in length and volume of the specimen when magnetized is, however, so small as to be negligible.

The curves obtained for intermediate orientations are given in fig. 5. The necessarily varying conditions of temperature under which the curves were taken will account for any slight irregularities in spacing. It should be noted that values of  $\frac{dR}{R}$  are in all cases plotted against the *external* field. The effect of polarity on the average value of the induction inside the specimen will of course increase as the specimen is rotated from the longitudinal to the transverse position, and this must be taken into account in making comparisons between the curves. It will be seen from the upper curves of the series that an error of setting of  $10^\circ$ , such as might arise when using wires 1 mm. long, would be sufficient to account for the greatest drop obtained by Owen.

It seems evident that the phenomena observed are closely connected with the changes of molecular configuration in the metal produced by the magnetic field. If in the case of the ferro-magnetic metals we take the quantity intensity of magnetization as some measure of these changes, we may note that the changes of resistance attain a maximum at about the strength of field at which the saturation value of the intensity is reached. Following the analogy of the

magnetization curve, we should expect the  $\frac{dR}{R}$  curve to attain a maximum, and not to fall after reaching that maximum, a result which would possibly be obtained under ideal experimental conditions, though it is not yet certain that the fall is not a real effect.

Fig. 5.



Adams \* has investigated the matter theoretically for the transverse field, developing the theory of J. J. Thomson, but assuming the collisions between corpuscles and atoms to be of the nature of those between hard elastic spheres.†

He obtains the expression

$$\frac{\partial R}{R} = \frac{\partial T}{T} - \frac{1}{4} H^2 \frac{e^2}{m^2} T^2,$$

where  $R$  is the resistance of the conductor with no magnetic field,  $\partial R$  the change of resistance in a field of strength  $H$ ,  $T$  the time of free path, and  $\partial T$  the change which the magnetic field produces in the free period through alteration of the molecular configuration. According to this theory, in order that the transverse magnetic field may produce an increase of resistance, it is necessary first that  $\partial T$  be positive, and secondly, that  $\frac{\partial T}{T}$  be greater than  $\frac{1}{4} H^2 \frac{e^2}{m^2} T^2$ .

\* Phys. Rev. xxiv. p. 428 (1907).



For the longitudinal field the expression

$$\frac{\partial R}{R} = \frac{\partial T}{T}$$

may be derived. It is pointed out by Heaps\* that “here  $\partial T$  is of somewhat broader significance than in the preceding formula. It includes the change of free period due to the altered path of the electron as well as the change due to modified molecular structure. A longitudinal field should thus produce a greater effect than a transverse field; and this is contrary to observed facts. By assuming that the molecular rearrangement due to a transverse magnetic field produces a greater increase of free period than that due to a longitudinal field, the two equations above can be taken as expressing experimental results.”

With reference to the difference between the effects for the longitudinal and transverse fields respectively, it may, however, be mentioned that for every specimen examined in the present case the effect for the longitudinal field was found to be markedly greater than that for the transverse field.

If, remembering the small magnitude of the current e.m.f., we assume that the molecular rearrangements due to the transverse and longitudinal fields respectively produce the same maximum value of  $\partial T$  in each case, we may obtain some idea of the order of magnitude of the free period of the electron in nickel.

Taking high values of the magnetic field in order to ensure saturation, and identifying  $H$  in the above equations with the magnetic induction  $B$ , we have from the above results for the longitudinal position

$$\frac{\partial T}{T} = \frac{\partial R}{R} = 23.47 \times 10^{-3},$$

where  $\partial T$  is the maximum change in  $T$  due to the longitudinal field,  $\partial R$  the maximum change in  $R$ .

For the transverse position

$$B = 17513; -\frac{\partial R}{R} = 13.9 \times 10^{-3};$$

taking the demagnetizing factor as  $2\pi$  and the saturation value of the intensity as 400.

\* *Loc. cit.* p. 906.

Hence, since

$$\frac{\partial R}{R} = \frac{\partial T}{T} - \frac{1}{4} H^2 \frac{e^2}{m^2} T^2,$$

we have

$$-13.9 \times 10^{-3} = 23.47 \times 10^{-3} - \frac{1}{4} (17513)^2 \cdot 10^{14} \cdot T^2,$$

whence

$$T = 2.2 \times 10^{-12} \text{ sec.}^*.$$

Indications seem to point to molecular and intermolecular effects of a highly complex nature, and until more definite information is available as to the structure of the molecule, it seems unlikely that a complete theory can be formulated.

In conclusion, we desire to express our obligation to Professor Taylor Jones, who suggested the research, for the valuable interest he has taken in the work, especially in the designing of the instrument employed in setting the specimen, the use of which has considerably enlarged the scope of the method.

Physics Laboratory,  
University College of N. Wales, Bangor,  
January 23rd, 1914.

LXXIV. *The Sum of an Infinite Series as the Solution of a Linear Differential Equation.* By I. J. SCHWATT †.

TO find

$$S = \sum_{n=0}^{\infty} \frac{r^n}{\prod_{m=1}^6 (n+m)} \dots \dots \dots (1)$$

Let  $u_n$  denote the  $(n+1)$ st term of the series, then

$$\frac{u_n}{u_{n-1}} = r \frac{n}{n+6},$$

or

$$(n+6)u_n = r n u_{n-1},$$

and

$$\sum_{n=1}^{\infty} (n+6)u_n = r \sum_{n=1}^{\infty} n u_{n-1} = r \sum_{n=0}^{\infty} (n+1)u_n$$

\* J. J. Thomson, in his 'Corpuscular Theory of Matter,' gives  $10^{-7}$  cm. as the order of magnitude of the free path of a corpuscle, and  $10^7$  cm. per sec. as that of the velocity, whence  $T = 10^{-14}$  sec.

† Communicated by the Author.

Adding

$$(n+6)u_n \Big]_{n=0} = \frac{1}{5!}$$

to both sides of the last equation,

we have

$$\sum_{n=0}^{\infty} (n+6)u_n = r \sum_{n=0}^{\infty} (n+1)u_n + \frac{1}{5!}.$$

But

$$\sum_{n=0}^{\infty} u_n = S \quad \text{and} \quad \sum_{n=0}^{\infty} nu_n = r \frac{dS}{dr},$$

therefore

$$r \frac{dS}{dr} + 6S = r^2 \frac{dS}{dr} + rS + \frac{1}{5!},$$

or

$$r(1-r) \frac{dS}{dr} + (6-r)S = \frac{1}{5!}. \quad . \quad . \quad . \quad (2)$$

Hence

$$\begin{aligned} S &= \frac{e^{-\int \frac{6-r}{r(1-r)} dr}}{5!} \int \left[ \frac{e^{\int \frac{6-r}{r(1-r)} dr}}{r(1-r)} + C \right] \\ &= \frac{1}{5!} \frac{(1-r)^5}{r^6} \left[ \int \frac{r^5}{(1-r)^6} dr + C \right]. \quad . \quad . \quad (3) \end{aligned}$$

Now

$$\begin{aligned} \int \frac{r^5}{(1-r)^6} dr &= \frac{r^5}{5(1-r)^5} - \frac{r^4}{4(1-r)^4} + \frac{r^3}{3(1-r)^3} - \frac{r^2}{2(1-r)^2} + \frac{r}{1-r} + \log(1-r) \\ &= \sum_{\kappa=1}^5 (-1)^{\kappa-1} \frac{r^{\kappa}}{\kappa(1-r)^{\kappa}} + \log(1-r). \quad . \quad . \quad . \quad (4) \end{aligned}$$

Therefore

$$S = \frac{1}{5!} \frac{(1-r)^5}{r^6} \log(1-r) + \frac{1}{5!} r \left[ \frac{1}{5} - \frac{1-r}{4r} + \frac{(1-r)^2}{3r^2} - \frac{(1-r)^3}{2r^3} + \frac{(1-r)^4}{r^4} \right]. \quad (5)$$

$$\begin{aligned} &= \frac{1}{5!} \frac{(1-r)^5}{r^6} \log(1-r) + \frac{1}{5!} r \left[ \left( 1 - \frac{1}{r} \right)^4 + \frac{1}{2} \left( 1 - \frac{1}{r} \right)^3 \right. \\ &\quad \left. + \frac{1}{3} \left( 1 - \frac{1}{r} \right)^2 + \frac{1}{4} \left( 1 - \frac{1}{r} \right) + \frac{1}{5} \left( 1 - \frac{1}{r} \right)^0 \right], \end{aligned}$$

$$= \frac{1}{5!} \frac{(1-r)^5}{r^6} \log(1-r) + \frac{1}{5!} r \sum_{\kappa=1}^5 \sum_{t=0}^{5-\kappa} (-1)^t \frac{\binom{5-t}{\kappa r^t}}{\kappa r^t}. \quad . \quad . \quad . \quad (6)$$

$$= \frac{1}{5!} \frac{(1-r)^5}{r^6} \log(1-r) + \frac{1}{5!} r \left[ \frac{137}{60} - \frac{77}{12r} + \frac{47}{6r^2} - \frac{9}{2r^3} + \frac{1}{r^4} \right]. \quad . \quad . \quad (7)$$

The same result might also be obtained by the following method.

The given series (1) can be written

$$S = \frac{1}{5!} \sum_{\kappa=1}^6 (-1)^{\kappa-1} \binom{5}{\kappa-1} \sum_{n=0}^{\infty} \frac{r^n}{n+\kappa}, \quad \dots \quad (8)$$

$$= \frac{1}{5!} \sum_{\kappa=1}^6 (-1)^{\kappa-1} \binom{5}{\kappa-1} \frac{1}{r^{\kappa}} \sum_{n=0}^{\infty} \frac{r^{n+\kappa}}{n+\kappa}, \quad \dots \quad (9)$$

$$= \frac{1}{5!} \sum_{\kappa=1}^6 (-1)^{\kappa-1} \binom{5}{\kappa-1} \frac{1}{r^{\kappa}} S_{\kappa}. \quad \dots \quad (10)$$

Then 
$$\frac{dS_{\kappa}}{dr} = \sum_{n=0}^{\infty} r^{n+\kappa-1} = \frac{r^{\kappa-1}}{1-r}. \quad \dots \quad (11)$$

Hence 
$$S_{\kappa} = \int_0^r \frac{r^{\kappa-1}}{1-r} dr + C_{\kappa}. \quad \dots \quad (12)$$

From (12) follows :

$$S_1 = \int_0^r \frac{dr}{1-r} = -\log(1-r);$$

$$S_2 = \int_0^r \frac{r dr}{1-r} = -\log(1-r) - r;$$

$$S_3 = \int_0^r \frac{r^2 dr}{1-r} = -\log(1-r) - r - \frac{r^2}{2};$$

$$S_4 = \int_0^r \frac{r^3 dr}{1-r} = -\log(1-r) - r - \frac{r^2}{2} - \frac{r^3}{3};$$

$$S_5 = \int_0^r \frac{r^4 dr}{1-r} = -\log(1-r) - r - \frac{r^2}{2} - \frac{r^3}{3} - \frac{r^4}{4};$$

$$S_6 = \int_0^r \frac{r^5 dr}{1-r} = -\log(1-r) - r - \frac{r^2}{2} - \frac{r^3}{3} - \frac{r^4}{4} - \frac{r^5}{5}.$$

From (10) we obtain :

$$\begin{aligned} S &= \frac{1}{5!} \sum_{\kappa=1}^6 (-1)^{\kappa} \binom{5}{\kappa-1} \frac{1}{r^{\kappa}} \log(1-r) + \frac{1}{5!} \sum_{\kappa=2}^6 (-1)^{\kappa} \binom{5}{\kappa-1} \frac{1}{r^{\kappa}} \sum_{t=1}^{\kappa-1} \frac{r^t}{t}, \\ &= \frac{(1-r)^5}{5! r^6} \log(1-r) + \frac{1}{5!} \sum_{\kappa=1}^5 \sum_{t=1}^{\kappa} (-1)^{\kappa+1} \frac{\binom{5}{\kappa}}{t r^{\kappa+1-t}}, \quad \dots \quad (13) \end{aligned}$$

$$= \frac{(1-r)^5}{5! r^6} \log(1-r) - \frac{1}{r 5!} \sum_{\kappa=1}^5 \sum_{t=1}^{\kappa} (-1)^{\kappa} \frac{\binom{5}{\kappa}}{t r^{\kappa-t}}, \quad \dots \quad (14)$$

$$= \frac{1}{5!} \frac{(1-r)^5}{r^6} \log(1-r) - \frac{1}{5! r} \left[ -\frac{137}{60} + \frac{77}{12r} - \frac{47}{6r^2} + \frac{9}{2r^3} - \frac{1}{r^4} \right], \quad \dots \quad (15)$$

which is the same result as (7).



Again, the summation of the given series might be effected by a method similar to the above but without the use of integration.

The given series can be written

$$S = \frac{1}{5!} \sum_{\kappa=0}^5 (-1)^{\kappa} \binom{5}{\kappa} \sum_{n=0}^{\infty} \frac{r^{n2}}{n + \kappa + 1}, \quad \dots \dots \dots (16)$$

$$= \frac{1}{5!r} \sum_{n=0}^5 (-1)^{\kappa} \binom{5}{\kappa} \frac{1}{r^{\kappa}} \sum_{n=0}^{\infty} \frac{r^{n+\kappa+1}}{n + \kappa + 1}.$$

Letting  $n + \kappa + 1 = t$ , we have

$$S = \frac{1}{5!r} \sum_{\kappa=0}^5 (-1)^{\kappa} \binom{5}{\kappa} \frac{1}{r^{\kappa}} \sum_{t=\kappa+1}^{\infty} \frac{r^t}{t}, \quad \dots \dots \dots (17)$$

$$= \frac{1}{5!r} \sum_{\kappa=0}^5 (-1)^{\kappa} \binom{5}{\kappa} \frac{1}{r^{\kappa}} \left[ \sum_{t=1}^{\infty} \frac{r^t}{t} - \sum_{t=1}^{\kappa} \frac{r^t}{t} \right],$$

wherein

$$\sum_{t=1}^0 \frac{r^t}{t} = 0.$$

Therefore

$$S = \frac{1}{5!r} \sum_{\kappa=0}^5 (-1)^{\kappa} \binom{5}{\kappa} \frac{1}{r^{\kappa}} \sum_{t=1}^{\infty} \frac{r^t}{t} - \frac{1}{5!r} \sum_{\kappa=1}^5 (-1)^{\kappa} \binom{5}{\kappa} \frac{1}{r^{\kappa}} \sum_{t=1}^{\kappa} \frac{r^t}{t} \quad \dots (18)$$

$$= -\frac{1}{5!r} \left(1 - \frac{1}{r}\right)^5 \log(1-r) - \frac{1}{5!r} \sum_{\kappa=1}^5 \sum_{t=1}^{\kappa} (-1)^{\kappa} \binom{5}{\kappa} \frac{r^t}{t r^{\kappa-t}}, \quad \dots (19)$$

$$= \frac{(1-r)^5}{5!r^6} \log(1-r) - \frac{1}{5!r} \sum_{\kappa=1}^5 \sum_{t=1}^{\kappa} (-1)^{\kappa} \binom{5}{\kappa} \frac{r^t}{t r^{\kappa-t}}. \quad \dots \dots \dots (20)$$

Which is the same result as obtained in (14).

University of Pennsylvania,  
Philadelphia, U.S.A.

LXXV. *The Influence of Volume Change on the Fluidity of Mixtures of Miscible Liquids.* By WILLIAM HOWIESON GIBSON\*.

SEVERAL formulæ have been used for the calculation of the fluidities or viscosities of mixtures of pairs of chemically indifferent, non-associated, completely miscible liquids from the fluidities or viscosities of the constituents,

\* Communicated by Sir William Ramsay, K.C.B., F.R.S.

but whatever formula is used it is exceptional to obtain values agreeing with experimental data.

Mixture formulæ based on percentages by weight of the constituents of the mixture have been used by Wijkander \*, Linebarger †, Thorpe and Rodger ‡, and Bingham §. Mixture formulæ based on percentages by volume have been used by Thorpe and Rodger, Lees ||, and Findlay ¶. Viscosity formulæ have been most used, but Bingham advocates fluidity formulæ on account of the parallelism between conductivity and fluidity.

The specific volume=fluidity formula of Batschinski\*\* for pure liquids, which has a rational basis and which gives excellent agreement with experiment, seems to give support to the use of a volume=fluidity formula for mixtures.

In this communication the fluidity formula of Lees is used,

$$F = V_1 F_1 + V_2 F_2,$$

where  $V_1$ ,  $V_2$  are the volumes of the two constituents in 1 c.c. of the mixture, and  $F$ ,  $F_1$ , and  $F_2$  are the fluidities of the mixture and the constituents.

As the composition of mixtures is usually expressed in percentages by weight, the formula is not convenient in the form given by Lees: a more convenient form is

$$100vF = m_1 v_1 F_1 + m_2 v_2 F_2,$$

where  $m_1$  and  $m_2$  are the percentages by weight of the constituents in the mixture;

$v_1$  and  $v_2$  the specific volumes of the constituents in the mixture, and  $v$  the specific volume of the mixture;

$F_1$  and  $F_2$  the fluidities of the constituents in the mixture, and  $F$  the fluidity of the mixture.

It is suggested that the above formula should hold for all mixtures of chemically indifferent, non-associated liquids, if  $v_1$  and  $v_2$  are understood to be the specific volumes assumed by the constituents of the mixture in the mixture, and not their specific volumes as pure liquids at the same temperature, while  $F_1$  and  $F_2$  are the fluidities corresponding to the

\* *Lunds. Phys. Sallsk. Jubelskrift*. 1878.

† *Amer. J. Sci.* (4) ii. p. 331 (1896).

‡ *J. C. S.* 1897, *Trans.* p. 360.

§ *Amer. Chem. Jour.* xxxv. p. 195 (1906).

|| *Phil. Mag.* (6) i. pp. 128-147 (1901).

¶ *Zeit. Phys. Chem.* lxix. p. 210 (1909).

\*\* *Zeit. Phys. Chem.* lxxxiv. p. 643 (1913).

specific volumes  $v_1$  and  $v_2$  as found experimentally, or as calculated from the formula of Batschinski :

$$v - w = cF,$$

where  $v$  is the specific volume of a liquid,  
 $w$  is the specific volume at zero fluidity,  
 $F$  is the fluidity, and  $c$  is a constant.

An hypothesis by the use of which the volume change of each constituent in a mixture can be calculated is required before the above fluidity formula can be used, and the values obtained by it compared with experimental data.

Lumsden \* examined the change in the molecular volume of solutes dissolved in organic solvents with change in temperature and concentration, and found that the molecular volume was affected by the temperature, concentration, and nature of the solvent.

These changes calculated on the assumption that the solvent is unaffected are too small, since any change in the volume of the solute will be accompanied by a change in the volume of the solvent.

Walden † considers that the molecular volume is connected with the co-volume of the solvent, holding that the greater the co-volume, the smaller is the solution volume of the solute.

The formula of Batschinski enables the value of  $w$ , which may be considered as the co-volume of a liquid, to be calculated for liquids from fluidity data, so that the relation between  $w$ , the co-volume, and  $v$ , the specific volume, for different liquids, may be compared.

The molecules of a liquid of volume  $Mw$  are free to move in the space  $Mv$ , where  $M$  is the molecular weight. On mixture with another liquid of different specific volume and co-volume, a rearrangement of the free space at the disposal of the molecules will usually occur until an equilibrium is reached ; that is to say, the specific volume of both liquids will change, and the change will depend on the concentration of each liquid in the mixture.

The hypothesis adopted in the calculations in this paper is that when two chemically indifferent, non-associated liquids are mixed their specific volumes change until the free space per unit of co-volume is the same for both kinds of molecule in the mixture. This would apply for any

\* J. C. S. 1907, Trans. p. 24.

† *Zeit. Phys. Chem.* lix. p. 385 (1907).

number of liquids, so that in a liquid mixture it is assumed that

$$\frac{v_1}{w_1} = \frac{v_2}{w_2} = \frac{v_3}{w_3} \dots \dots \frac{v_n}{w_n},$$

where  $v_1 \dots$  is the specific volume taken up by the constituent in the mixture, and

$w_1 \dots$  is the co-volume of the constituent.

For this assumption to be true, all liquids, non-associated and chemically indifferent, which have the same ratio of  $v$  to  $w$  at the same temperature, should undergo no volume change on mixing, and the fluidities of mixtures of the two liquids should be given by the formula

$$100 vF = m_1 v_1 F_1 + m_2 v_2 F_2.$$

Carbon tetrachloride and benzene are two such liquids. Batschinski's formula for carbon tetrachloride is

$$v - 0.5782 = 0.000475 F ;$$

for benzene it is

$$v - 1.0476 = 0.000581 F ;$$

therefore

$$\frac{w_1}{w_2} = \frac{0.5782}{1.0476} = 0.552.$$

The following table gives the ratio of  $v_{\text{CCl}_4}$  to  $v_{\text{C}_6\text{H}_6}$  for temperatures from  $10^\circ \text{C.}$  to  $70^\circ \text{C.}$ —

Temperature.	$v_{\text{CCl}_4}$ .	$v_{\text{C}_6\text{H}_6}$ .	$v_1/v_2$ .
10° C.	0.6199	1.1242	0.552
20	0.6274	1.1377	0.552
30	0.6350	1.1514	0.552
40	0.6428	1.1661	0.552
50	0.6510	1.1812	0.551
60	0.6594	1.1966	0.551
70	0.6683	1.2124	0.551

It follows that the ratio of  $v$  to  $w$  is the same for carbon tetrachloride and benzene at all temperatures from  $10^\circ \text{C.}$  to  $70^\circ \text{C.}$ , and there should be no change in volume on mixing these two liquids.

Thorpe and Rodger found a very slight contraction, decreasing with rise of temperature.

Again, the fluidities found for mixtures between  $10^\circ \text{C.}$



and 70° C. should agree with the fluidities calculated from the formula

$$100 vF = m_1 v_1 F_1 + m_2 v_2 F_2.$$

The following table compares Thorpe and Rodger's results with the calculated values:—

Temp. ° C.	Mixture I. 77.63 CCl <sub>4</sub> .		Mixture II. 56.21 CCl <sub>4</sub> .		Mixture III. 32.29 CCl <sub>4</sub> .	
	found	F calc.	found	F calc.	found	F calc.
10	100	103.3	110.2	113.7	120.2	122.8
20	117.6	120.6	129.0	133.0	141.5	143.6
30	136.3	139.0	149.0	153.2	163.5	165.5
40	156.0	158.7	171.5	175.0	186.6	189.0
50	176.7	178.9	195.0	197.2	211.5	213.0
60	199.0	200.4	219.5	220.9	237.0	238.3
70	...	...	243.5	245.5	264.0	265.2

It can be seen that the agreement is fairly good.

For the same pair of liquids Ramsay and Aston \* found that surface tension followed the mixture rule; and J. von Zawidski † found only a slight deviation of the vapour-pressure curve from the mixture rule, this deviation being later ascribed to slight association of carbon tetrachloride by Dolezalek ‡.

It may be pointed out here, that of the liquid mixtures which give straight-line vapour-pressure curves investigated by J. von Zawidski, benzene and ethylene dichloride, the only pair for which the Batschinski equation of each liquid is known, have the same ratio of  $v$  to  $w$ , and from that standpoint would be expected to behave normally.

A second pair of liquids fully investigated by Thorpe and Rodger was methyl iodide and carbon bisulphide.

Batschinski's formula for methyl iodide is

$$v - 0.3804 = 0.000284 F,$$

and for carbon bisulphide

$$v - 0.6642 = 0.000471 F.$$

\* *Zeit. Phys. Chem.* xv. p. 92 (1894).

† *Zeit. Phys. Chem.* xxxv. p. 129 (1900).

‡ *Zeit. Phys. Chem.* lxiv. p. 727 (1908).

In this case,  $\frac{w_1}{w_2} = 0.5727$  ;

at 0° C.,  $\frac{v_1}{v_2} = 0.5535$ ,

at 40° C.,  $\frac{v_1}{v_2} = 0.5544$ ,

*i. e.*, at the same temperatures the specific volumes and the co-volume are not in the same ratio for the two liquids. A change in volume is to be expected, and is actually found.

On the hypothesis that in any mixture of these two liquids the free space per unit of co-volume becomes the same for both kinds of molecule, the specific volumes taken up by each liquid in any mixture can be calculated.

Let  $v_1$  be the volume taken up in the mixture by 1 gram of methyl iodide, and  $w_1$  its co-volume ;

$v_2$  the volume taken up in the mixture by 1 gram of carbon bisulphide, and  $w_2$  its co-volume.

Let  $v$  be the specific volume of the mixture.

Let  $m_1$  be the percentage by weight of methyl iodide.

$m_2$  be the percentage by weight of carbon bisulphide.

$$\text{Then} \quad \frac{v_1}{w_1} = \frac{v_2}{w_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$100 v = m_1 v_1 + m_2 v_2. \quad . \quad . \quad . \quad . \quad (2)$$

The values of the unknowns  $v_1$  and  $v_2$  can be found by substitution.

By substituting these values in the Batschinski equations, the fluidities of each constituent in the mixture can be found.

The value of the fluidity for the mixture can then be found from the formula

$$100 vF = m_1 v_1 F_1 + m_2 v_2 F_2,$$

and compared with the experimental value.

The following table gives the calculated and Thorpe and Rodger's experimental values for five mixtures at different temperatures, and shows that the calculated values agree with the experimental values within the experimental error.

Ether and chloroform, a third pair of liquids investigated by Thorpe and Rodger, were shown by Dolezalek \* to combine

\* *Zeit. Phys. Chem.* lxxi. p. 191 (1910).

668 *Influence of Volume Change on Fluidity of Mixtures.*

Temp.	$v$	$v_1$	$v_2$	$F_1$	$F_2$	F calc.	F found.
Mixture I. $m_1$ 78·4, $m_2$ 21·6.							
0° C.	0·504	0·434	0·758	189·1	198·9	192·3	193·1
10	0·510	0·439	0·767	207	218	211·1	211·6
20	0·516	0·444	0·776	225·4	237·2	229·2	231·0
30	0·523	0·450	0·786	246·5	259·7	250·8	250·8
40	0·5295	0·456	0·796	266·2	280·3	270·8	271·1
Mixture II. $m_1$ 61·19, $m_2$ 38·81.							
0	0·565	0·438	0·765	203·2	214	208·9	207·6
10	0·5712	0·443	0·773	220·1	231·8	226·2	225·7
20	0·578	0·448	0·783	238·7	251·4	245·4	244
30	0·5853	0·454	0·793	258·7	272·3	265·8	263·2
40	0·5927	0·460	0·803	279·0	293·8	286·7	282·8
Mixture III. $m_1$ 51·89, $m_2$ 48·11.							
0	0·596	0·439	0·766	204·8	215·6	211·5	213·3
10	0·603	0·444	0·775	223·2	235·2	230·6	230·0
20	0·610	0·449	0·784	241·1	253·8	249	248·2
30	0·618	0·455	0·794	261·3	275·4	270·1	268
40	0·626	0·460	0·804	281·7	296·6	290·9	286
Mixture IV. $m_1$ 31·19, $m_2$ 68·81.							
0	0·667	0·441	0·770	213·6	224·8	222·5	223
10	0·675	0·446	0·779	232·0	244·4	241·9	242
20	0·683	0·452	0·789	250·8	264·1	261·3	262
30	0·692	0·457	0·798	270·1	284·5	281·6	281
40	0·700	0·463	0·808	290·0	305·3	302·2	300
Mixture V. $m_1$ 17·61, $m_2$ 82·39.							
0	0·715	0·442	0·773	218·7	230·4	229·1	228·4
10	0·723	0·448	0·782	236·7	249·3	247·8	248
20	0·731	0·453	0·7909	255·3	269·0	267·4	268
30	0·740	0·458	0·800	273·9	288·7	287·1	288
40	0·749	0·464	0·810	293·7	309·6	307·7	309·5

to a considerable extent ; there are three constituents in the mixture, and as nothing is known about the fluidity of the compound no calculation can be made.

The hypothesis advanced in this paper may therefore be said to harmonize well with the careful experimental work of Thorpe and Rodger.

LXXXVI. *On the Integration of the Differential Equation applicable to a Plane Progressive Wave.* By J. ROSE-INNES, M.A., B.Sc.\*

**L**ORD RAYLEIGH in his 'Theory of Sound' has given the differential equation applicable to a plane progressive wave as

$$\left(\frac{dy}{dx}\right)^2 \frac{d^2y}{dt^2} = \frac{dp}{dx} \frac{d^2y}{dx^2} \quad (\text{vol. ii. p. 32}).$$

He quotes Earnshaw's trial solution

$$\frac{dy}{dt} = F\left(\frac{dy}{dx}\right),$$

and also Earnshaw's final conclusion that the integral of the equation is to be found by eliminating  $\alpha$  between the equations

$$\begin{aligned} y &= \alpha x + F(\alpha)t + \phi(\alpha), \\ 0 &= x + F'(\alpha)t + \phi'(\alpha). \end{aligned}$$

This form of integral, however, does not lend itself readily to the introduction of the initial conditions, and I therefore think it of some interest to present another solution of the equation which enables us to impose the initial conditions with more facility.

From Earnshaw's trial solution we readily obtain

$$\frac{d^2y}{dt^2} = \left\{ F'\left(\frac{dy}{dx}\right) \right\}^2 \frac{d^2y}{dx^2}.$$

In order that this may coincide with the original differential equation, we have to choose  $F$  so as to fulfil the condition

$$\left\{ F'\left(\frac{dy}{dx}\right) \right\}^2 \left(\frac{dy}{dx}\right)^2 = \frac{dp}{dx};$$

and since

$$\frac{dy}{dx} = \frac{\rho_0}{\rho},$$

we may write the condition

$$\left\{ F'\left(\frac{\rho_0}{\rho}\right) \right\}^2 \left(\frac{\rho_0}{\rho}\right)^2 = \frac{dp}{d\rho}.$$

\* Communicated by the Author.



670 Mr. J. Rose-Innes on *Integration of the Differential*  
 Earnshaw's trial solution may also be written

$$u = F\left(\frac{\rho_0}{\rho}\right)$$

if for shortness we denote the term  $\frac{dy}{dt}$  by  $\bar{u}$ .

Differentiate with regard to  $\rho$ ,

$$\frac{du}{d\rho} = -F'\left(\frac{\rho_0}{\rho}\right)\frac{\rho_0}{\rho^2},$$

$$\begin{aligned}\left(\frac{du}{d\rho}\right)^2 &= \left\{F'\left(\frac{\rho_0}{\rho}\right)\right\}^2 \frac{\rho_0^2}{\rho^4} \\ &= \frac{1}{\rho^2} \frac{d\rho}{d\rho}.\end{aligned}$$

Hence

$$\frac{du}{d\rho} = \frac{1}{\rho} \sqrt{\frac{d\rho}{d\rho}}.$$

Then since

$$\frac{du}{dt} = \frac{du}{d\rho} \frac{d\rho}{dt},$$

we have

$$\begin{aligned}\frac{d\rho}{dt} &= \frac{du}{dt} \div \frac{du}{d\rho} \\ &= -\frac{1}{\rho_0} \frac{d\rho}{dx} \div \frac{du}{d\rho} \\ &= -\frac{1}{\rho_0} \frac{d\rho}{d\rho} \frac{d\rho}{dx} \div \frac{1}{\rho} \sqrt{\frac{d\rho}{d\rho}} \\ &= -\frac{\rho}{\rho_0} \sqrt{\frac{d\rho}{d\rho}} \cdot \frac{d\rho}{dx}.\end{aligned}$$

Now

$$\begin{aligned}d\rho &= \frac{d\rho}{dx} dx + \frac{d\rho}{dt} dt \\ &= \frac{d\rho}{dx} \left\{ dx - \frac{\rho}{\rho_0} \sqrt{\frac{d\rho}{d\rho}} \cdot dt \right\}.\end{aligned}$$

Thus  $d\rho = 0$  if  $dx$  and  $dt$  are so related that  $dx = \frac{\rho}{\rho_0} \sqrt{\frac{d\rho}{d\rho}} dt$ .

The velocity  $\frac{\rho}{\rho_0} \sqrt{\frac{d\rho}{d\rho}}$  occurring in the last equation will be that of a plane moving as the wave moves so as to occupy successively the undisplaced position of those particles which

at any moment constitute the part of the wave characterized by the density  $\rho$ .

Suppose  $y = \psi(x)$  initially,

then  $\frac{dy}{dx} = \psi'(x)$  initially;

and from what has been proved above we shall have at any subsequent time

$$\frac{dy}{dx} = \psi' \left( x - \frac{\rho}{\rho_0} \sqrt{\frac{dp}{d\rho}} \cdot t \right).$$

This equation gives us  $\rho$  when  $x, t$ , and the function  $\psi$  are all known; but we note that it will not be possible in general to exhibit  $\rho$  as an explicit function of  $x$  and  $t$ .

Again, since

$$\frac{du}{d\rho} = \frac{1}{\rho} \sqrt{\frac{dp}{d\rho}},$$

we shall have

$$u + \rho \frac{du}{d\rho} = u + \sqrt{\frac{dp}{d\rho}};$$

so that

$$\frac{d}{d\rho} u \rho = u + \sqrt{\frac{dp}{d\rho}}.$$

Imagine a plane at which the density is always  $\rho$  travelling along with the disturbance; then by taking account of the constancy of the mass within a specified small distance on each side of the plane, its velocity is readily seen to be  $\frac{d}{d\rho} \rho u$ .

Thus the value of  $\rho$  at time  $t$  for particles whose disturbed position is given by  $y$  will be the same as the value of  $\rho$  at the beginning of the disturbance for particles whose disturbed position differs by  $\left(u + \sqrt{\frac{dp}{d\rho}}\right)t$ . We have already seen above that the undisturbed position of the particles corresponding to  $\rho$  at time  $t$  will differ by  $\frac{\rho}{\rho_0} \sqrt{\frac{dp}{d\rho}} \cdot t$  from the initial position. Hence

$$y - \left(u + \sqrt{\frac{dp}{d\rho}}\right)t = \psi \left( x - \frac{\rho}{\rho_0} \sqrt{\frac{dp}{d\rho}} \cdot t \right),$$

or

$$y = \psi \left( x - \frac{\rho}{\rho_0} \sqrt{\frac{dp}{d\rho}} \cdot t \right) + \left(u + \sqrt{\frac{dp}{d\rho}}\right)t.$$

The result of eliminating  $\rho$  between this last equation and

$$\frac{dy}{dx} = \psi' \left( x - \frac{\rho}{\rho_0} \sqrt{\frac{dp}{d\rho}} \cdot t \right)$$

may be regarded as the integral of the original differential equation, satisfying the conditions imposed.

The two moving planes which we have considered above in connexion with a part of the disturbance at density  $\rho$  have been shown to travel in general with unequal velocities. It is worth noting, however, that the difference in the velocities involves only small quantities of the second order. Thus

$$\begin{aligned} u + \sqrt{\frac{dp}{d\rho}} &= \sqrt{\frac{dp}{d\rho}} + \int_{\rho_0} \sqrt{\frac{dp}{d\rho}} \cdot \frac{d\rho}{\rho} \\ &= \sqrt{\frac{dp}{d\rho}} + \int_{\rho_0} \rho \sqrt{\frac{dp}{d\rho}} \cdot \frac{d\rho}{\rho^2} \\ &= \sqrt{\frac{dp}{d\rho}} + \left( \frac{1}{\rho_0} - \frac{1}{\rho} \right) M, \end{aligned}$$

where  $M$  is some mean value of  $\rho \sqrt{\frac{dp}{d\rho}}$  between the limits of the integral. Again,

$$\begin{aligned} \frac{\rho}{\rho_0} \sqrt{\frac{dp}{d\rho}} &= \sqrt{\frac{dp}{d\rho}} + \frac{\rho - \rho_0}{\rho_0} \sqrt{\frac{dp}{d\rho}} \\ &= \sqrt{\frac{dp}{d\rho}} + \left( \frac{1}{\rho_0} - \frac{1}{\rho} \right) \rho \sqrt{\frac{dp}{d\rho}}. \end{aligned}$$

The quantities  $M$  and  $\rho \sqrt{\frac{dp}{d\rho}}$  differ by a small quantity, and they are each multiplied by the factor  $\left( \frac{1}{\rho_0} - \frac{1}{\rho} \right)$  which is itself small.

If we put the two velocities equal, we are led to the same relation between pressure and density as Rankine found necessary to secure the propagation of a wave of permanent type. The mere fact that the two planes will in general travel with different speeds can be proved by quite elementary considerations.

LXXVII. *On the Formation of Images by means of an Opaque Disk.* By ALFRED W. PORTER, F.R.S., University College, London\*.

[Plate IX.]

**I**N spite of the prominence given in treatises on Physical Optics to the existence of the bright spot at the centre of the shadow formed by a point-source and a circular disk, it does not seem to have been recognized that, as ordinarily exhibited, the bright spot is in reality an image of the source of light. The source is never a point-source in practice, and the contour of the bright patch is simply the locus of the diffraction spots formed by the various points on the contour of the source of light. I have for some years been impressed by the very sharp boundary of the bright spot when obtained by means of a pinhole source; a sharpness quite inconsistent with one's expectations from the account usually given. It was only a few weeks ago that it occurred to me that the explanation is that the theoretical bright spot is much smaller than the patch of light obtained. To test this I took in the first place a circular source about 9 mm. in diameter, with a thin wire stretched across its centre, illuminated from behind by an electric arc, and found as I suspected that the spot was transformed into a sharp image of the bright opening with its dark bar. We have thus the possibility of obtaining sharp images of small objects, *using an opaque disk instead of a lens*. In conjunction with Mr. E. Talbot Paris, I have taken photographs of a triangular opening; one of these is reproduced (Pl. IX.).

The size of the true bright spot is easily obtained theoretically for a source on the axis of the disk.

The intensity at any point Q distant  $r$  from the axis is given by

$$I = \frac{(V_1^2 + V_0^2)}{(a+b)^2},$$

where 
$$V_1 = \frac{z}{y} J_1(z) - \frac{z^3}{y^3} J_3(z) + \text{etc.},$$

$$V_0 = J_0(z) - \frac{z^2}{y^2} J_2(z) + \text{etc.},$$

$$y = \frac{2\pi(a+b)c^2}{ab\lambda},$$

and 
$$z = \frac{2\pi rc}{\lambda b}.$$

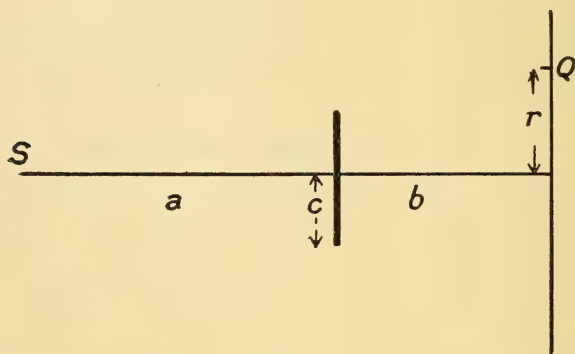
The maxima and minima are given by  $V_0 J_1 = 0$ . The

\* Communicated by the Author.



first minimum following the central maximum is given by  $V_0=0$ .

Taking, in illustration, the data for the case of the photograph which is reproduced, we have  $a=63$  cm.,  $b=170$  cm.,  $c=.44$  cm.  $\lambda=.00005$  cm.; whence the value of  $y$  (which is independent of the point Q) is  $83\pi$ . Lommel has calculated the values of  $V_0$  as far as  $y=8\pi$  only; but in our case it is unnecessary to calculate them



further because the vanishing of  $V_0$  practically coincides with the vanishing of  $J_0$ , as  $z/y$  is then exceedingly small and  $J_0$  is changing fast. This occurs when  $z=2.40$ ; the corresponding value of  $r$  is  $.0074$  cm. Hence the whole of the bright spot must be within this radius and the visible part of it may be considerably within.

For points of an extended source which lie off the axis, the above formula no longer, in strictness, applies; but it may still be used approximately for points sufficiently near to the axis. The corresponding bright spot is then on the secondary axis through the centre of the disk, and the distance of the spot from the principal axis is given by the ordinary law of transverse magnification in geometrical optics, *i. e.* width of image/width of object  $= b/a$ . In the above numerical case, the length of each side of the triangular source was  $.21$  cm., and of the image was  $.58$  cm. This latter is nearly 40 times as long as the diameter of the bright spot. It may be pointed out that this ratio is independent of  $b$ , and is inversely proportional to  $a$ ; there is therefore an advantage in placing the disk fairly near to the source.

Contrast should be drawn between the optical definition in this case and in the complementary case of pinhole photography. It would be impossible to have obtained a photograph of the triangle with an aperture of the same size instead of a disk.

LXXVIII. *The Theory of X-Ray Reflexion. Part II. By*  
 C. G. DARWIN, M.A., *Lecturer in Mathematical Physics in*  
*the University of Manchester\**.

1. **I**N the First Part of this paper† formulæ were obtained giving the intensity of reflexion of X-rays by a crystal, and by a discussion of the results of experiment‡ it was concluded that a factor had been neglected which in fact must be of some importance, and that to represent the case at all accurately an improved theory was necessary. It was indicated that the factor to be included is the influence of the vibration of each atom on that of the others. If this is not done, cases will present themselves in which the conservation of energy is apparently violated. The experiment which was discussed is one of these cases. In the present paper this mutual influence is allowed for and a revised formula is found for the reflexion from a crystal. Comparison with experiment shows that the new formula is no better able than the old to account for the observed strength of reflexion. It appears, however, that this may be attributed to the fact that in all crystals there is a considerable amount of distortion, so that there are a great many separate small regions in which reflexion takes place. As a consequence of this fact it will be deduced that, constant factors apart, the old reflexion formulæ may be allowed to stand. We shall first of all deal with the reflexion from a perfect crystal.

2. *Reflexion from one Plane.*

In the earlier work the procedure was first to calculate the reflexion from a single plane of atoms and then to combine the effects of the different planes. The amplitude of the reflexion from one plane was represented by a coefficient  $-iq$ , where  $q$  is made up in the following way. A wave of unit amplitude and length  $2\pi/k$  falls on an atom. Let  $f(\psi, k) e^{-ikr}/r$  be the amplitude of the wave it scatters, measured at a distance  $r$  in a direction inclined at angle  $\psi$  to the direction of the incident wave. In addition to  $\psi$  and  $k$ ,  $f$  will depend on the direction of polarization of the incident wave. Let  $N$  be the number of atoms per c.c. (for the present we shall suppose them all identical) and  $a$  the distance between successive planes; then  $Na$  is the areal density

\* Communicated by Prof. Sir Ernest Rutherford, F.R.S.

† Darwin, *Phil. Mag.* vol. xxvii. p. 315 (1914).

‡ *Loc. cit.* p. 331.

of atoms in a plane. Let  $\theta$  be the glancing angle between the direction of incidence and the plane. Then \*

$$q = \frac{2\pi N a f(2\theta, k)}{k \sin \theta} \dots \dots \dots (1)$$

As long as the atoms are supposed not to influence one another's motion, every plane however deep in the crystal scatters the same amount of radiation, and if no allowance were made for the absorption of the transmitted wave the reflexion would become indefinitely large. Now an atom in rocksalt may be supposed to have about 10 electrons, and so  $f$  is probably about  $10 \frac{e^2}{mc^2} \dagger$ . Taking  $N = 4.50 \times 10^{22}$ ,

$a = 2.81 \times 10^{-8}$  and reflexion in the first order so that  $k \sin \theta = \pi/a$ , we find that  $q$  is about  $2 \times 10^{-4}$ . According to the assumptions of the earlier paper, the amplitude of the wave is reduced by absorption in passing through one plane by an amount  $\frac{1}{2} \mu a \operatorname{cosec} \theta$ , and for soft X-rays this is  $4 \times 10^{-6}$ . Thus we should expect reflexion to be much more efficient than absorption in extinguishing the transmitted wave. Indeed, we shall find that over a certain small range of angles of incidence the reflexion is practically complete and does not depend on the absorption coefficient.

In the earlier paper the coefficient of reflexion  $q$  was calculated by considering a spherical wave coming from a point source. In view of the greater complexity of the present problem it is more convenient to deal with plane waves, and we must therefore first observe that the evaluation of  $q$  could have been done equally well with these. It is only necessary to find the amplitude of reflexion at a point so distant from the crystal, that in the principal part of the field the phases of waves from adjacent atoms are sensibly the same—this permits the summation to be replaced by an integration—while yet the point is not so distant that the crystal has to be regarded as finite—this introduces the Fresnel factors in the integral and makes it converge. There can be little doubt that the procedure gives the right value, though it is not of course mathematically rigorous. It has the great advantage that the formulæ do not involve the exact number of atoms in the whole plane, which is obviously quite irrelevant to the final results.

The formula for  $q$  cannot be quite general, if  $f$  is supposed to depend only on the atom itself. For we might then make

\* *Loc. cit.* pp. 319–320.

† *Loc. cit.* pp. 326–329.

$N_a$ , the areal density of atoms, so large that the conservation of energy would be violated. In nature this is of course obviated by the fact that if the atoms are too closely crowded together, the wave from each will influence the others. We have seen that for rocksalt  $q$  is only of the order  $10^{-4}$ , so that the conservation of energy is in no danger, and we shall continue to use  $q$  as it stands. The direct calculation of the influence of all the atoms on one of their number leads to a double series of some complexity. I am informed by a friend\* to whom I referred the matter, that the series does in general converge (which was not at all obvious at first sight), but that the question is quite a difficult problem in pure mathematics. I do not give the form of the series as no use is to be made of it. It will be found that the forces from the other atoms exert an effect like an addition to the radiation term in the vibration of an electron. The radiation term hardly influences the amplitude of vibration of an electron under the influence of X rays (except in the case of resonance), and so we may conclude that the mutual influence of the atoms in a plane may be neglected.

When a wave falls on a single plane of atoms, besides the directly reflected wave there are others scattered. Thus there will be a wave given off in any direction for which a line of atoms are in phase together, while the next parallel line is a phase  $2\pi$  behind. These diffracted waves are destroyed by the operation of the other planes of the crystal; but there remains a wave scattered in the same direction as the transmitted beam. The amplitude of this wave is given by  $-iq_0$ , where  $q_0$  is obtained from  $q$  by replacing  $f(2\theta, k)$  by  $f(0, k)$ . As was shown in the earlier work, it is the wave  $-iq_0$  which gives rise to the refractive index†.

### 3. Combination of Planes.

The difficulty of the problem of allowing for the mutual influence of the atoms in one plane is the complete absence of phase relations between the waves arriving at one atom from the rest, but this is also the reason why it is justifiable to neglect it. For the combination of all the planes the matter is quite otherwise. Here, when the radiation is at the angle of reflexion, all the waves reflected from the successive planes are in phase together, and they must be supposed to give rise to a secondary reflexion, which

\* Mr. G. H. Hardy, F.R.S., of Trinity College, Cambridge, to whom I must express my thanks for his kind interest in the question.

† *Loc. cit.* p. 320.



contributes a component in the direction of the transmitted wave. It was this secondary reflexion that was neglected in the earlier work, on the assumption that the radiation scattered by one atom had no effect on the others. The recombination into a single wave of the wavelets from the atoms in one plane will not be very complete in the short distance between adjacent planes, but the error in assuming it complete will not be systematic. Moreover, the mutual influence of two planes alone is very small; it is only the cumulative effect that is important. We thus have a problem very similar to that of the Fabry-Perrot étalon, only with an infinite number of parallel equidistant plates.

We shall suppose that independently of the scattering of the atoms there is also a small absorption. Thus if a plane wave  $e^{ik(Ct-x\cos\theta+z\sin\theta)}$  falls on a single plane of atoms, the reflected wave is  $-iq e^{ik(Ct-x\cos\theta-z\sin\theta)}$  and the transmitted wave is  $(1-h-iq) e^{ik(Ct-x\cos\theta+z\sin\theta)}$ . The term  $h$  represents the absorption and may be taken as  $\frac{1}{2}\mu a \operatorname{cosec} \theta$ .

We consider a crystal composed of atoms of a single substance arranged in planes at distance  $a$ . Let  $T_r$  represent in amplitude and phase the total transmitted wave just above the  $(r+1)$ th plane,  $S_r$  the total reflected wave in the same position. Then  $T_0$  is the incident wave, and  $S_0$  the reflected wave.  $S_r$  is derived from two components, the part of  $T_r$  reflected by the  $r+1$ th plane and the part of  $S_{r+1}$  transmitted through it. The latter must be multiplied by a phase factor  $e^{-ika\sin\theta}$  to give its value just below the  $r+1$ th plane instead of just above the  $r+2$ th. Thus

$$S_r = -iqT_r + (1-h-iq_0) e^{-ika\sin\theta} S_{r+1}.$$

Again  $T_{r+1}$  is made up of the part of  $T_r$  transmitted through the  $r+1$ th plane and the part of  $S_{r+1}$  reflected by it. Putting in the proper phase factors we have

$$T_{r+1} e^{ika\sin\theta} = (1-h-iq_0) T_r - iq e^{-ika\sin\theta} S_{r+1}.$$

If we eliminate the  $S$ 's from these difference equations we obtain

$$(1-h-iq_0) e^{-ika\sin\theta} (T_{r-1} + T_{r+1}) = [1 + q^2 e^{-2ika\sin\theta} + (1-h-iq_0)^2 e^{-2ika\sin\theta}] T_r,$$

and the solution is given by  $T_r = T_0 x^r$ , where  $x$  is the root of

$$(1-h-iq_0) e^{-ika\sin\theta} \left(x + \frac{1}{x}\right) = 1 + q^2 e^{-2ika\sin\theta} + (1-h-iq_0)^2 e^{-2ika\sin\theta} \dots \quad (2)$$

The product of the roots of this equation is unity and that one is to be taken which makes  $|x| < 1$ . Otherwise the intensity would increase with  $r$ . If we substitute back with this solution we find

$$S_r = T_0 \frac{-iqx^r}{1 - x e^{-ika \sin \theta} (1 - h - iq_0)},$$

and in particular

$$\frac{S_0}{T_0} = \frac{-iq}{1 - x e^{-ika \sin \theta} (1 - h - iq_0)}. \quad \dots (3)$$

This expression holds for any angle of incidence.

We shall now approximate by allowing for the fact that  $q$ ,  $q_0$ ,  $h$  are small and by supposing that the incident wave is very nearly at the angle of best reflexion. Then  $\theta$  is very near  $\phi$ , where  $ka \sin \phi = n\pi - q_0$ . The presence here of  $q_0$  represents the shift in the angle of best reflexion due to the refractive index, as explained in the former paper\*. We have then

$$ka \sin \theta = n\pi - q_0 + v,$$

where

$$v = ka \cos \phi (\theta - \phi). \quad \dots (4)$$

To the degree of approximation needful we have

$$e^{-ika \sin \theta} = (-)^n (1 + iq_0 - iv),$$

so that

$$\frac{S_0}{T_0} = \frac{-iq}{1 - (-)^n x (1 - h - iv)}$$

and  $x$  is that root of

$$(-)^n (1 - h - iv) \left( x + \frac{1}{x} \right) = 1 + q^2 + (1 - h - iv)^2,$$

for which  $|x| < 1$ .

The roots of this equation are very nearly  $(-1)^n$ , so to solve it we put  $x = (-)^n (1 - \epsilon)$ .

Substituting in the equation we have

$$(1 - h - iv)(2 + \epsilon^2) = 1 + q^2 + (1 - h - iv)^2,$$

so that

$$\epsilon = \sqrt{\{q^2 + (h + iv)^2\}}.$$

The ambiguity is to be determined so that the real part is positive. Thus

$$\frac{S_0}{T_0} = \frac{-iq}{h + iv + \sqrt{\{q^2 + (h + iv)^2\}}}. \quad \dots (5)$$

\* *Loc. cit.* p. 318.

The earlier paper was written under an assumption which may be seen to be equivalent to taking  $q$  much smaller than

$h$ , so that  $\frac{S_0}{T_0} = \frac{-iq}{2(h+iv)}$  \*. It is quite possible to evaluate

the expressions required with any values of  $h$  and  $q$ , but the formulæ involve elliptic functions, so that their numerical values are not easy to see. Now as we saw  $q$  is probably about  $2 \times 10^{-4}$  while  $h$  is only  $4 \times 10^{-6}$ , so that not much error is introduced by supposing  $h/q$  negligible. It would not, however, have been permissible to have supposed that  $h$  vanished at the beginning of the work, because if this were done it would be found that for some angles the reflexion tends to no definite value as the number of planes tends to infinity.

In discussing the ambiguity of  $\sqrt{q^2 + (h+iv)^2}$  when  $h$  vanishes it will be convenient to suppose  $q$  positive. We do not know whether this is true, but if  $q$  is really negative the modification is very simple. When  $-q < v < q$  we have simply  $\sqrt{q^2 - v^2}$ , the positive square root being taken. When  $v > q$  we must write the expression in the form  $\pm i\sqrt{(v^2 - q^2 - 2ivh)}$ , and if the radicle is expanded it will be seen that the proper value is  $+i\sqrt{(v^2 - q^2)}$ . Without the presence of  $h$  this could not have been determined. Similarly when  $v < -q$  we have to take  $-i\sqrt{(v^2 - q^2)}$ . Thus the amplitude of reflexion is

$$\left. \begin{aligned} & -\frac{q}{v - \sqrt{(v^2 - q^2)}} \quad \text{for } v < -q \\ & -\frac{q}{v - i\sqrt{(q^2 - v^2)}} \quad \text{for } -q < v < q \\ & -\frac{q}{v + \sqrt{(v^2 - q^2)}} \quad \text{for } q < v \end{aligned} \right\} \dots \quad (6)$$

To express the intensity of reflexion we take the moduli of the squares of these quantities. In the middle region this is unity and reflexion is perfect. Now  $v = ka \cos \phi(\theta - \phi)$ , so this is the region

$$\theta = \phi \pm s, \text{ where } s = q/ka \cos \phi.$$

If we take the reflexion in the first order of rocksalt for the platinum radiation  $\beta$  ( $\lambda = 1.11 \times 10^{-8}$  cm.) we find  $s = 3''$ . For the second order it is about half this.

On account of the perfect reflexion the transmitted wave

\* This is equivalent to one of the equations on p. 322 of the earlier paper.

is rapidly extinguished. Since  $\frac{T_r}{T_0} = x^r = (-)^{nr} e^{-r \sqrt{q^2 - v^2}}$  it follows that at a depth  $z$  in the crystal the intensity is only  $\exp -2 \frac{z}{a} \sqrt{q^2 - v^2}$  of its value at the surface, and so we may speak of an extinction coefficient

$$\frac{2}{a} \sqrt{q^2 - v^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Averaged across the whole region of perfect reflexion this gives a coefficient

$$4q/\pi a. \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

For the value of  $q$  which we have been using, this gives about 8000, whereas the absorption coefficient, taken as  $\mu \operatorname{cosec} \phi$ , is for the platinum rays only 300. Thus the extinction is complete long before the rays going in a slightly different direction are appreciably absorbed. This fact is important in explaining the reflexion from an ordinary imperfect crystal.

#### 4. Spherical Wave and Effect of a Slit.

We have so far only dealt with plane waves. A spherical wave can be made by compounding together in an integral a set of equal plane waves going in all different directions. If we put in the reflexion factor for each of these plane waves, we obtain an integral representing the diffraction pattern of the reflected beam. At the distances at which experiments are usually made this pattern would be of some complexity. Since it would never be observed in practice on account of the finite area of any actual source and the imperfection of the crystal, it is unnecessary to discuss it. To find the whole intensity of reflexion we may examine the effect at infinity. Here the waves are all plane, so that we can apply the formulæ (6) direct. If we take the intensity at a point at glancing angle  $\phi + \epsilon$ , we have  $r = ka \cos \phi \cdot \epsilon$ . So, making use of the abbreviation  $s = q/ka \cos \phi$ , we find as the intensity at a great distance  $\rho$

$$\left. \begin{array}{ll} \frac{1}{\rho^2} \cdot \frac{s^2}{(\epsilon - \sqrt{\epsilon^2 - s^2})^2} & \text{when } \epsilon < -s \\ \frac{1}{\rho^2} \cdot 1 & \text{when } -s < \epsilon < s \\ \frac{1}{\rho^2} \cdot \frac{s^2}{(\epsilon + \sqrt{\epsilon^2 - s^2})^2} & \text{when } s < \epsilon \end{array} \right\} \cdot \quad . \quad . \quad (9)$$



Suppose that the intensity of the monochromatic incident beam at a distance  $R$  is  $I/R^2$ , and that the whole effect is observed in an instrument having a slit of length  $l$  and sufficient breadth to include the whole beam. Then the instrument will measure

$$I \frac{l}{\rho} \left\{ \int_{-\infty}^{-s} \frac{s^2 d\epsilon}{(\epsilon - \sqrt{\epsilon^2 - s^2})^2} + 2s + \int_s^{\infty} \frac{s^2 d\epsilon}{(\epsilon + \sqrt{\epsilon^2 - s^2})^2} \right\},$$

which reduces to

$$I \frac{l}{\rho} \frac{8}{3} s.$$

If we put in the value of  $s$  this reduces to

$$I \frac{l}{\rho} \frac{8}{3\pi} N |f(2\phi, k)| \lambda^2 \operatorname{cosec} 2\phi. \quad \dots (10)$$

Of the two polarized components that for which the electric vibration is in the plane of incidence has in its  $f$  a factor  $\cos \phi$  \*. Introducing this and also the temperature factor † we have

$$I \frac{l}{\rho} \frac{8}{3\pi} \frac{1 + |\cos 2\phi|}{2} N |f| e^{-\frac{1}{2} \frac{kT}{\sigma a^2} (2n\pi)^2} \lambda^2 \operatorname{cosec} 2\phi. \quad (11)$$

As in the earlier paper, we next find the result of limiting the incident beam by a slit. To describe the diffractive effect of a slit it is usual to imagine that every point of the slit gives out a spherical wave, and that the separate waves are coherent. For our purpose it is better to resolve the waves from the slit into a set of plane waves. The amplitude of any of these waves is given by a Fresnel integral taken between the proper limits. The amplitude of reflexion in any direction will be determined by the product of this Fresnel integral and the reflexion factor for the corresponding direction. Let the slit be at a distance  $r$  from the source and of angular breadth  $\sigma$ . Then we saw in the earlier paper ‡ that the intensity opposite the centre of the slit has practically its full value when  $\sigma^2 \frac{kr}{\pi} = 6$ , and so if the slit is placed

symmetrically with regard to the reflexion, the intensity of reflexion has its full value at the central point. If we take  $k = 10^9$  and  $r = 30$  cm. this gives  $\sigma = 5''$ . Now we know that

\* *Loc. cit.* p. 323.

† *Loc. cit.* p. 325. The expression used is not applicable to low temperatures.

‡ *Loc. cit.* p. 323.

the breadth of the good reflexion is  $6''$  and if we calculate the intensity corresponding to a slit of the supposed breadth at  $3''$  from the centre, we find it to be a little less than that at the centre. So we conclude that a slit of  $5''$  will hardly give full reflexion. As the breadth is only required for the purpose of a rough estimate, we shall take it at  $8''$ . This is the narrowest slit which can be used if the intensity of reflexion of monochromatic rays is not to suffer.

### 5. White Radiation.

We next find the intensity of reflexion of white radiation. Let the intensity of the incident radiation at distance  $R$  from the source be  $\frac{1}{R^2} \int_0^\infty u dk$ . Reflexion only occurs for values of  $k$  near those which satisfy the equation  $ka \sin \theta = n\pi - q_0$ . These values will be denoted by  $k_n$ . A value of  $k$  near  $k_n$  can be expressed in the form  $k = k_n \left(1 + \frac{x}{n\pi}\right)$ . The centre of best reflexion for  $k$  is at an angle  $\theta - \eta$  where

$$ka \sin (\theta - \eta) = n\pi - q_0,$$

and it follows from this that  $x = ka \cos \theta \cdot \eta$ , so that  $x$  is the same as  $v$  in (6). The intensity of reflexion thus is

$$\frac{1}{\rho^2} \sum_n u_n \frac{k_n}{n\pi} \left\{ \int_{-\infty}^{-q} \frac{q^2}{(x - \sqrt{x^2 - q^2})^2} dx + 2q + \int_q^\infty \frac{q^2}{(x + \sqrt{x^2 - q^2})^2} dx \right\},$$

$$\text{or} \quad \frac{1}{\rho^2} \sum u_n \frac{k_n}{n\pi} \frac{8}{3} q.$$

If we introduce the value of  $q$  and the factors for polarization and temperature, and if we express the result in terms of the quantity  $E_\lambda$  where  $E_\lambda d\lambda = u dk$ , we have

$$\frac{1}{\rho^2} \frac{16}{3\pi} \frac{1 + |\cos 2\theta|}{2} N a^2 \sum_n \frac{1}{n^2} e^{-\frac{1}{2} \frac{kT}{\sigma a^2} (2n\pi)^2} (|f| E_{\lambda\lambda})_n. \quad (12)$$

### 6. Composite Crystal.

When the crystal is composite the complete discussion of any special case is rather more complicated. If, for example, the alternate planes are different in character, we obtain a set of four difference equations involving two different types of T's and S's. If three of these are eliminated we obtain a single difference equation for the fourth, the solution of

which depends on a quadratic equation rather more complicated than (2). The subsequent procedure follows the same course as in § 3. The general problem, though straightforward, might be rather complicated, but by the following argument is made unnecessary. The influence of a single atom on another is always very minute, and the effect only becomes important by its repeated recurrence. Consequently no error will be introduced by regarding as the unit of scattering, not the atom, but the group of atoms in a single unit of the crystal lattice. Let  $f_r$  be the scattering of an atom of type  $r$ , of which there are  $N_r$  per c.c., and let this atom occur at distance  $\alpha_r a$  from the first plane,  $a$  being the distance in which the structure of the crystal repeats itself. Then in the reflexion formulæ the expression

$$N |f| e^{-\frac{1}{2} \frac{k_T}{\sigma a^2} (2n\pi)^2}$$

must be replaced by

$$\left| \sum_r N_r f_r e^{-i2n\pi\alpha_r} e^{-\frac{1}{2} \frac{k_T}{\sigma_r a^2} (2n\pi)^2} \right|^*.$$

### 7. Comparison with Experiment.

We now compare our result with experiment, and to do so shall take the same experiment as was discussed in the former paper†. The elimination of the higher orders of reflexion follows the same course as before, but the numbers resulting measure now not  $E_\lambda \frac{\lambda^2}{\mu}$  but  $E_\lambda \lambda$ . We thus obtain revised values of  $E_\lambda$ . I do not give the details, because we shall see that a further modification is necessary in the reflexion formula. The quadrature of  $E_\lambda$  now gives that

$$E_0 \lambda_0 = 1.3 \int E_\lambda d\lambda,$$

where  $E_0, \lambda_0$  refer to the wave-length  $3.92 \times 10^{-9}$  cm. which is reflected by rocksalt at  $4^\circ$ . We have seen that all the reflexion occurs in a region of about  $8''$  and is practically perfect in this region, so we estimate the efficiency for the reflexion in rocksalt at  $4^\circ$  as  $E_0 \frac{d\lambda}{d\theta} \delta\theta / \int E_\lambda d\lambda$  where  $\delta\theta = 8''$ .

Using the quadrature this becomes  $1.3 \cot 4^\circ \cdot \delta\theta$  or  $0.0004$ . The observed efficiency is  $0.0035$ , and this calculated value is no better than the old one.

\* See the earlier paper, p. 325.

† *Loc. cit.* p. 330.

In spite of their failure to account for the amount of reflexion, the formulæ developed here are to be preferred to the earlier ones, since they include an effect which has been shown to have been unjustifiably disregarded in the former paper. The new formulæ make the reflexion independent of the absorption coefficient of the crystal. Now the work of W. H. Bragg\* has proved that absorption does play an important part in the reflexion, and this suggests a way out from the discrepancy. If a crystal is not perfect, so that the planes are not everywhere absolutely parallel, it may happen that some part of the beam which has not been extinguished by reflexion at the surface will find a piece of the inside of the crystal at the proper angle, and so will give rise to a second reflexion. Such an effect will obviously involve the absorption coefficient of the rays in the crystal.

### 8. *Imperfect Crystal.*

The irregularity of a crystal is of necessity a rather indefinite matter, which it would be perhaps difficult to discuss with rigour. We shall only attempt to see the general type of change to be expected. We will first study the effect of supposing that the surface is irregular, without taking into account the possibility of interior reflexions. Suppose that the surface is divided up into a number of plates whose normals all point in slightly different directions. It is clear that in some cases there might be no reflexion or there might be several. Now the rays reflected from two different plates of the crystal will travel in slightly different directions, and if a photographic plate is put in their path they will strike it at different points. But if the distance of the photographic plate from the crystal is the same as that of the source, they will strike it at the same point; for on account of the constancy of the angle of reflexion, the locus of points which can reflect rays from a given source to a given point is a circle, and only when source and point are equidistant from it does this circle touch the crystal. In this case only is there any considerable area on the crystal which can all reflect to the same point. Moreover, as we shall see later, a very important fraction of the reflected radiation comes from reflexions inside the crystal, and these will be focussed to points only very slightly different from those coming from the surface. The accuracy with which Moseley† could determine his X-ray spectra is probably partly due to this

\* W. H. Bragg, *Proc. Roy. Soc. A.* vol. lxxxix. p. 430 (1914).

† Moseley, *Phil. Mag.* vol. xxvi. p. 1024 (1913).



focussing, since (though for a different reason) his photographic plate and source were at the same distance from the crystal.

It is quite possible that a given crystal surface should systematically reflect more than its due share of radiation. For example, if it were of a wavy form, each separate wave would reflect a ray. But we can show that on the average there is no improvement in the reflexion when the surface is supposed divided into small plates, the normals of which deviate from their mean direction in a random manner. In such an indefinite question as the present it is useless to proceed with any great rigour, and we shall be content with a rather general argument. In the first place, there is no need to allow for the fact that the normals of the plates deviate from the plane of incidence of the rays. The only effect of this is to shift the ray to a different part of the line of reflected rays. In considering the reflexion from a set of plates, the normals of which all lie in the plane of incidence, it will be sufficient to take it that a ray is reflected to the full extent given in (11), when a line can be drawn from the source to the plate, making exactly an angle  $\phi$ , the reflexion angle, with its plane. For a plate in any fixed position on the crystal there will be a certain small range of directions of the normal such that a line can be drawn from a given source to make angle  $\phi$  with the plate. This range is limited by the two positions when the line cuts the plate at either of its two edges, and therefore the range of inclinations of the plate which can give a reflexion is proportional to its breadth. The chance of a reflexion is thus not altered by cutting the plate in half, for if this is done either of the halves must be aimed in the proper direction with just twice the accuracy, that is to say each half is just half as likely to give a reflexion. Thus there is on the average the same probable number of reflexions when the crystal is broken into many plates as when it is broken into few, or finally as when it is perfect. We conclude that there is no average improvement or deterioration of reflexion when the surface of the crystal is broken up.

When we come to consider the inside of the crystal the matter is quite different. We saw in § 3 that if the crystal is perfect all the radiation that can be reflected, is so, long before the depth at which rays at a different angle are appreciably absorbed. Now if the crystal is twisted internally these unabsorbed rays may come on a part of it at the right angle, and so give rise to a second reflexion. We must estimate how this will affect the matter. Suppose  $d$  to be a

depth such that the crystal is twisted through an amount sufficient to allow of a new reflexion. Roughly speaking, then, at every successive  $d$  we shall get a reflexion, and the intensities of these reflexions will be 1,  $e^{-2\mu d \operatorname{cosec} \phi}$ ,  $e^{-4\mu d \operatorname{cosec} \phi}$ , &c. The whole reflexion formula should then be multiplied

by  $\frac{1}{1 - e^{-2\mu d \operatorname{cosec} \phi}}$ , or  $\frac{1}{2\mu d \operatorname{cosec} \phi}$  if the crystal is so badly

twisted that there are a number of reflexions. It appears that as it describes a property of the crystal,  $d$  ought to be taken constant. For a not very great distortion this might be justifiable, but we have strong experimental reason to believe that the crystals are even more imperfect than this. For when the reflexion is evaluated with this factor it will be found that the second order of reflexion is as strong as the first, a result known to be untrue. This must be taken to indicate that crystals are so badly twisted that their planes do not remain parallel even long enough to produce a single perfect reflexion.

Suppose, therefore, that the crystal is composed of pieces each of depth  $d$  small compared with the amount necessary to produce a perfect reflexion. At the depth  $d$  the transmitted wave has on the average an intensity  $e^{-4qd/\pi a}$  (see (8)), and the wave reflected by the thickness  $d$  has intensity

$1 - e^{-4qd/\pi a}$  or  $\frac{4qd}{\pi a}$ . Suppose one of the reflecting pieces is

at depth  $z$ . Then the amount reflected from it is propor-

tional to  $\frac{4qd}{\pi a} e^{-2\mu z \operatorname{cosec} \phi}$ . The number of such pieces in a

length  $dz$  is  $dz/d$ , so that the reflexion formula is to be multiplied by a factor

$$\frac{4qd}{\pi a} \int_0^\infty e^{-2\mu z \operatorname{cosec} \phi} dz/d \text{ or to } \frac{2}{\pi a} \frac{q \sin \phi}{\mu}.$$

If we multiply (11) and (12) by this we see that apart from a numerical factor they lead to the old expressions for the reflexion\*. That this should be so is not remarkable, since each reflecting piece of the crystal consists only of a few planes, so that the mutual influence of the atoms becomes unimportant. The chief difference is that the whole reflexion now no longer takes place in a band  $5''$  broad, so that the argument† which pointed to the insufficiency of the earlier formulæ loses its validity. The displacement of the reflexion

\* *Loc. cit.* pp. 332, 334.

† *Loc. cit.* p. 331.

due to refraction remains, since the distortion of the crystal does not influence the phase relations of the waves scattered in the direction of the transmitted beam. The pattern observed on a photographic plate will in general be very irregular, but when the plate and source are equidistant from the crystal it should have the general character of a band one side of which shades off exponentially. It is readily calculated that the intensity in the band falls to a fraction  $1/e$  in a breadth  $\sin \phi \cos \phi / \mu$ .

For convenience I repeat the reflexion formulæ.

The effect of monochromatic radiation measured in an instrument at distance  $\rho$  from the image of the source with a slit of length  $l$  and sufficient breadth is

$$I \frac{l}{\rho} A \frac{1 + \cos^2 2\phi}{2} N^2 \frac{f^2}{\mu} e^{-\frac{KT}{\sigma a^2} (2n\pi)^2} \frac{1}{2} \lambda^2 \operatorname{cosec} 2\phi \dots (13)$$

The intensity of reflexion of white radiation is

$$\frac{A}{\rho^2} \frac{1 + \cos^2 2\theta}{2} N^2 a^2 \sum_n \frac{1}{n^2} e^{-\frac{KT}{\sigma a^2} (2n\pi)^2} \left( \frac{f^2 E \lambda^2}{\mu} \right)_n \dots (14)$$

The factor  $A$  will probably vary from crystal to crystal according to the amount of contortion, but we should not expect it to depart widely from unity, its value in the earlier paper. As we are now free from the argument about the limitation of reflexion to a breadth of  $5\lambda$ , we may use the experimental value of the efficiency to determine  $f^2$ . When  $A$  was unity it was found to be  $26(e^2/mC^2)^2$ , and this is of the order to be expected from atoms with about 10 electrons, of which some, but not all, are concentrated close together.

### 9. *Scattering from a Single Atom.*

Since the first part of this paper was written two experimental results have been published by W. L. Bragg†, which have an important bearing on our subject. In the first place he has shown that we must suppose that each atom scatters a wave whose amplitude is proportional to its atomic weight. Thus in fluorspar the two fluorine atoms give waves which can destroy by interference the wave coming from one calcium atom. Since all experiments have shown that the atomic weight is proportional to the number of electrons  $\nu$  in the atom, we conclude that  $f$  is closely proportional to  $\nu$ . This result would hold if we could suppose that the majority

\* *Loc. cit.* p. 331.

† W. L. Bragg, *Proc. Roy. Soc. A*, vol. lxxxix. p. 468 (1914).

of the electrons were crowded together in a region of the order of  $10^{-9}$  cm., and this they certainly will be for the heavier elements. But if this is so there is a certain amount of difficulty with regard to Bragg's second experimental result. From measurements of crystals of a good many substances, he concludes that on the average the relative strengths of reflexion of the several orders for monochromatic radiation are as the numbers 100, 20, 7, 3, 1. After allowing for the temperature corrections these numbers are fairly well expressed by the formula  $\frac{1}{n^2}$ ; but since the radiation is not appreciably dispersed they are to be compared not with (14) but with (13), and in this formula the reflexion is proportional to  $\frac{1}{n}$ . Thus, we must attribute a factor  $\frac{1}{n}$  to  $f^2$ , the coefficient for the scattering of a single atom. Now we saw in the earlier paper\* that  $f^2$  will certainly decrease with the order of reflexion, and the expression there found seems capable of accounting for the excess scattering from amorphous substances, as in this case experiments have only been concerned with light atoms where there is no great concentration of electrons; but when we are dealing with heavier atoms we have seen that Bragg's first result points to a considerable crowding of electrons in a small space, and in this case it would hardly be expected that the excess effect should be so great as to give a factor  $\frac{1}{n}$ . Involving as it does a knowledge of the arrangement of the electrons in the atom, it does not seem possible at present to make any better progress in discussing this question.

#### Summary.

The paper attempts a more accurate solution than was given in the first part of the problem of X-ray reflexion, on the basis of allowing for the mutual influences of the scattering atoms.

(i.) It is shown that the mutual influences of the atoms in a plane together are unimportant.

(ii.) The interactions of the separate planes are allowed for, and revised reflexion formulæ are deduced. The reflexion is found to be practically perfect for a certain range of angles. The transmitted beam is extinguished much

\* *Loc. cit.* p. 329.



more rapidly than corresponds to the true absorption of the crystal.

(iii.) Comparison with experiment suggests that the new formulæ can account for the observed intensity as little as the old.

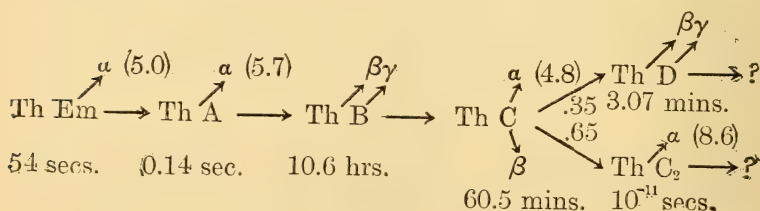
(iv.) This observed strength of reflexion is to be attributed to crystalline imperfection, and allowing for this the old formulæ of the first part are retained with a new numerical factor.

My thanks are due to Prof. Sir Ernest Rutherford for the kind interest he has taken in this research.

March 4, 1914.

LXXIX. *The Transformations in the Active Deposit of Actinium.* By E. MARSDEN, M.Sc., *Lecturer in Physics,* and P. B. PERKINS, Ph.D., *University of Manchester*.\*

IT is well known that the "C" products of the active deposits of radium and thorium are anomalous in that in both cases the atom has two distinct modes of transformation, *i. e.* it breaks up with emission of either an  $\alpha$  or a  $\beta$  particle. In the case of thorium C, owing to the fact that the chance of disintegration in either of the two ways is of the same order, it has been found possible to examine the process in considerable detail, and the following scheme of transformation has been arrived at†:—

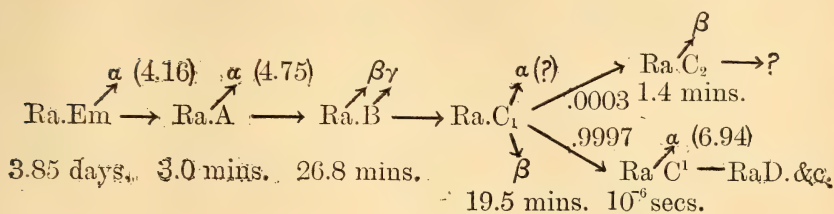


By analogy the method of production of the branch product,  $\text{C}_2$ , has been deduced‡.

\* Communicated by Sir E. Rutherford, F.R.S.

† Marsden & Barratt, *Proc. Phys. Soc.* xxiv. 1, p. 50 (1911); Marsden & Darwin, *Proc. Roy. Soc. A.* lxxxvii. p. 17 (1912); Marsden & Wilson, *Phil. Mag.* xxvi. p. 354 (1913).

‡ K. Fajans, *Phys. Zeit.* xii. p. 369 (1911); xiii. p. 699 (1912).



From the close analogy of the thorium and actinium series it is to be anticipated that actinium C should also show two modes of disintegration, and the present experiments were made to test this point\*.

It will be noticed, in the cases of both thorium C and radium C, that the branch disintegration involves the emission of a long-range  $\alpha$  particle, 8.6 cm. in the former case and 6.94 cm. in the latter. Further, with the whole series of products in equilibrium, the total number of  $\alpha$  particles of the two ranges emitted by the "C" products is equal to the number from the emanation and A products on the main series. From the experiments of Geiger† such a result must also hold for actinium C if a branch occurs in this product.

Experiments were consequently made to test whether any long-range  $\alpha$  particles were emitted from actinium C, the general evidence indicating that the number of such particles must be small compared with the number of range 5.4 cm., which constitute the main radiation‡. The simplest method of making such an experiment would be to take a source of actinium active deposit, and to count the scintillations on a zinc sulphide screen placed in air at different distances from it. Such an experiment had already been tried by Geiger§, and we have repeated it without finding any  $\alpha$  particles beyond 5.4 cm. However, with the sources of actinium available the number of  $\alpha$  particles falling on an area of 1 sq. mm. (the area of the field of the microscope) at distances greater than 5 cm. is very small. Consequently, a sheet of mica of air equivalent over 5 cm. was interposed between

\* The first part of these experiments was carried out by R. H. Wilson and one of us, and the results were given briefly in 'Nature,' xcii. p. 29 (Sept. 11, 1913).

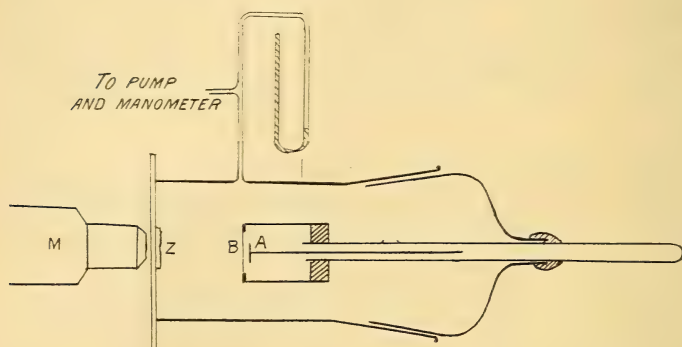
† Geiger, Phil. Mag. xxii. p. 201 (1912).

‡ Cf. R. Swinne, Phys. Zeit. xiv. p. 142 (1913).

§ Geiger, loc. cit.

the source and screen so that a smaller distance between the two could be used. The arrangement is shown in fig. 1.

Fig. 1.

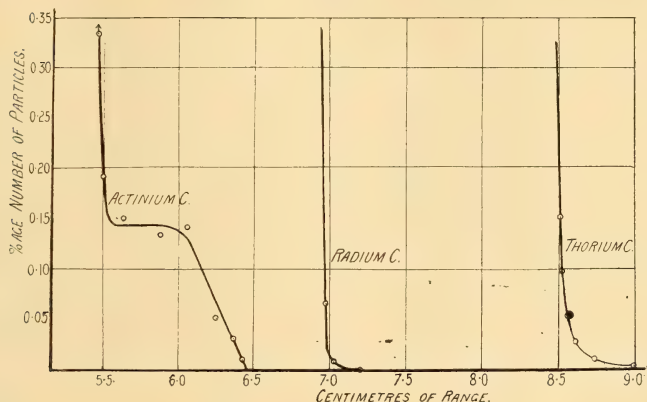


The  $\alpha$  particles from the source A passed through a sheet of mica B and impinged on the zinc-sulphide screen Z, where the scintillations were observed by a microscope M. The distance of A to Z could be varied in different experiments, and was generally between 0.9 and 1.5 cm. The thickness of mica was also varied in different experiments between 5 and 7 cm. air equivalent. The pressure of air in the apparatus was measured by a manometer, and thus the equivalence of the distance AZ could be expressed in terms of air at 15° C. and 76 cm. By adding the equivalent of the mica the "range" at which the  $\alpha$  particles were counted could thus be determined.

The procedure in an experiment was generally as follows:— A was exposed for several hours to a source of actinium emanation and then placed in a convenient position inside the apparatus with a sheet of mica of known thickness placed over it. Countings of the scintillations were then made at different air-pressures for about 40 minutes, in which time the source had decayed to less than half value. A was then removed and the total number of  $\alpha$  particles emitted measured by counting the scintillations on a zinc-sulphide screen placed at a known distance in a completely exhausted apparatus. From the known decay of the actinium active deposit all the measurements could be corrected to the initial time, and thus the percentage of particles reaching any "range" could be determined. The curve marked "Actinium C" in fig. 2 gives the results of a particular experiment. The other curves give the results of exactly similar experiments with radium C and thorium C<sub>2</sub> respectively; in the latter case account has been

taken of the fact that only 65 per cent. of the  $\alpha$  particles of thorium C have a range 8.6 cm.

Fig. 2.



It will be seen that the curve for actinium C differs from the others, and indicates that about 0.15 per cent. of the particles can penetrate much further than the ordinary  $\alpha$  particles of range 5.4 cm.

The effect is very small and exact measurement is difficult. With the source used the maximum number of scintillations per minute due to the long-range  $\alpha$  particles was seldom more than 20 per minute even when corrected to the initial time, *i. e.* for the maximum activity of the source. Consequently not more than about 40 scintillations could in general be counted for any one point on the curve, and this brings in very considerable probability variations. However, the number of  $\alpha$  particles corresponding to the flat part of the curve between 5.5 and 5.9 cm. range only varied in ten experiments between 0.10 and 0.20 per cent., which is well within the experimental error and the error due to probability. The mean ratio found was 0.15 per cent., and the range of the new  $\alpha$  particles or the range at which scintillations cease to be produced was about 6.4 cm.

Various experiments were tried to make sure that the long-range  $\alpha$  particles were not due to radium C or thorium C which might come from a small quantity of radium or radiothorium in the source. In the case of radium C it is known that its decay for a long exposure is not much different from that of actinium. The absence of radium C in the source was, however, proved by the fact that the ratio of long-range  $\alpha$  particles was not altered when the plate A was exposed to



the actinium preparation for two hours, or for several days, in a completely closed vessel. In the latter case the radium emanation would accumulate and give a far greater quantity of radium C than for a two-hours exposure. Further, the agreement between the various experiments in giving the range as 6.4 cm. in itself shows that no radium C  $\alpha$  particles of range 6.9 cm. were present. Difficulty was, however, experienced in the earlier experiments from thorium C as an impurity. This was shown by the presence of  $\alpha$  particles of range 8.6 cm., the number of which did not decay at the same rate as the actinium active deposit, but with the well-known period of thorium B, 10.6 hours. The number of these particles was with long exposures about 0.03 per cent. of the initial number of  $\alpha$  particles from actinium C, but by exposing for only two hours the number could be considerably reduced and the small necessary correction could be made by counting the number of scintillations at a range greater than 6.4 cm. In the curve given in fig. 1 the thorium C  $\alpha$  particles only amounted initially to 0.005 per cent., and have been corrected for.

Since the range of the observed  $\alpha$  particles differs little from that of actinium A, *i. e.* 6.5 cm., it might be thought possible that they may be due to this product derived from actinium X obtained by recoil from the actinium in the source. The nearly constant ratio obtained in the experiments and the rate of decay of the number of long-range  $\alpha$  particles, however, negative this idea.

The above experiments therefore indicate that the  $\alpha$  particles of actinium C are complex, and that 0.15 per cent. have a range of 6.4 cm., while the *main* number have a range of 5.4 cm.

*Ionization Curves of  $\alpha$  Particles from Polonium, Actinium C, Radium C, and Thorium C.*

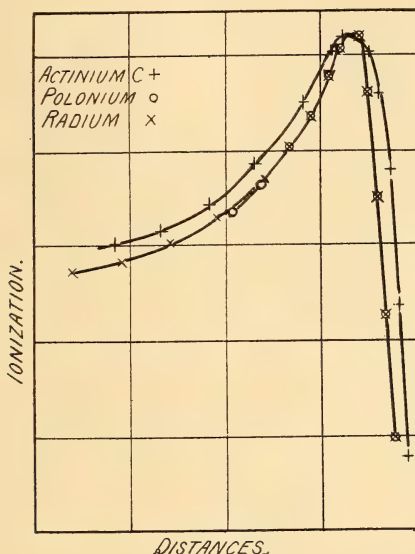
In connexion with these experiments it must be recalled that Mlle. Blanquies\* in 1909 came to the conclusion that two  $\alpha$  ray products are present in the active deposit of actinium. This conclusion was based mainly on a comparison of the ionization curves for polonium, actinium C, and radium C. The ionization curves obtained are reproduced in fig. 3.

It will be noticed that although the curves for polonium and radium C are superposable, the curve for actinium C shows a much less pronounced "knee," as though complex

\* Mlle. Blanquies, *Le Radium*, vi. p. 230 (1909); vii. p. 159 (1910).

$\alpha$  particles were present. It is obvious, moreover, that the difference between the curves is much more than could be accounted for by such a small fraction of long-range  $\alpha$  particles as found above; indeed these particles would

Fig. 3.

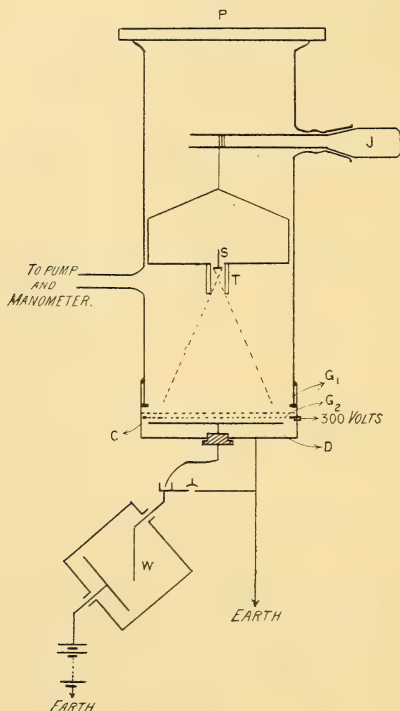


have no detectable influence on the ionization curve as ordinarily determined. Consequently we have repeated the experiments and determined the ionization curves for polonium, actinium C, radium C, and thorium C. Our experiments do not confirm her results, yet they have brought to light some interesting points in connexion with ionization curves, and they will therefore be described at length.

The apparatus used is shown in fig. 4, and is essentially the same as the well-known Bragg apparatus, except that the source was moved by a ground-glass joint J instead of through a stuffing-box. The source S was placed in a narrow brass tube T which could be moved vertically inside the wide glass tube. Consequently a narrow pencil of  $\alpha$  particles was directed normally through two wire gauzes  $G_1$  and  $G_2$  on to the electrode.  $G_1$  was connected to the brass cylinder C which was also connected to earth.  $G_2$  was insulated from C by a ring of mica, and was connected to a battery of 320 volts, the other terminal of which was earthed. The electrode D was connected to a sensitive Wilson-Kaye

electroscope W. The current observed in the latter was thus due to the ionization produced by the  $\alpha$  particles in the shallow space between  $G_2$  and D, which was 3 mm. in depth, and by altering the distance of the source an ionization curve

Fig. 4.



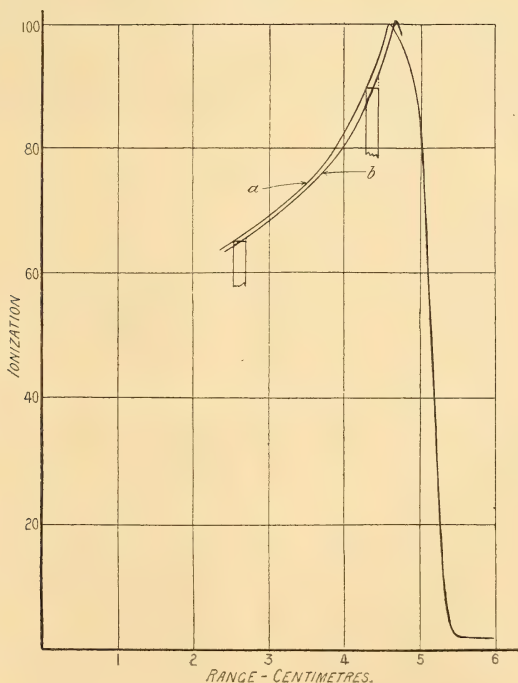
could be obtained. The electrode D had a diameter of 6 cm. and the brass tube T an internal diameter of 10 mm. The glass tube B was waxed air-tight to the brass cylinder so that the whole apparatus could be exhausted and any desired pressure used, the source being introduced through a ground-glass plate P. For radium C, actinium C, and thorium C, small well-polished metal disks of diameter about 4 mm. were exposed to the respective emanations; as source of polonium an equal-sized sheet of platinum was used, which had been activated with radium (D + E + F) by repeated exposure to large quantities of radium emanation about two years ago. The surface of the platinum was bright and not contaminated in any way.

In the experiments with the various substances the pressure

was adjusted in each case so that the range of the  $\alpha$  particles was practically the same, viz. 9 cm. Thus for the experiment with polonium, the range of whose  $\alpha$  particles is known to be 3.77 cm. at  $15^{\circ}\text{C}$ . and 76 cm. Hg :—The temperature in a particular experiment was  $17^{\circ}\text{C}$ ., and thus the pressure required inside the apparatus was  $76 \times \frac{3.77}{9.0} \times \frac{273+17}{273+15} = 32.0$ . Subtracting this from the barometric height 75.3 cm. gives 43.3 cm. as the required difference of level of the two limbs of the manometer.

In this way curves were obtained under exactly similar circumstances as regards configurations of the apparatus. To compare the shapes of the curves they were reduced to the same scale of pressure, viz. 76 cm. and  $15^{\circ}\text{C}$ . Thus in the case of actinium the curve marked (a) in fig. 5 was calculated as

Fig. 5.



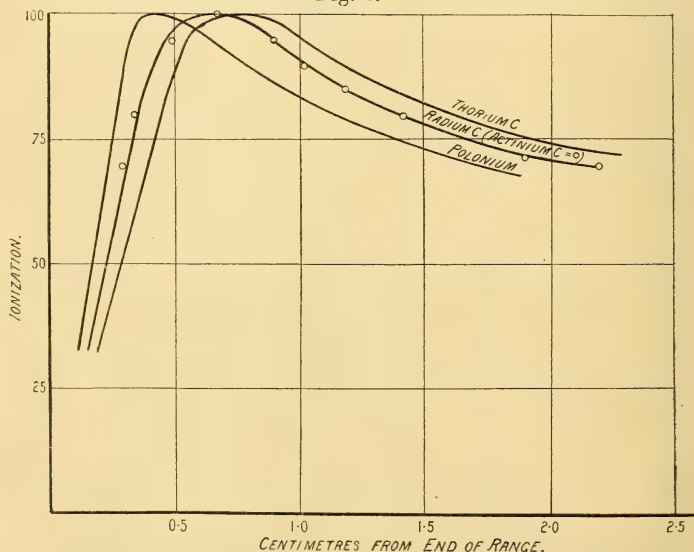
the mean of several curves, and similarly for the other substances. For a strict comparison of the curves another correction is necessary, namely, that for the finite depth of the ionization chamber. This depth was 0.3 cm., and thus



the ionization measured for any given distance, say  $x$  cm., of the source to the first gauze  $G_1$  really represents the integral of the curve between  $x$  and  $x + 0.3$  cm. In the curve reduced to  $15^\circ$  C. and 76 cm. Hg. (fig. 5 a) this would correspond to the integral between  $y \cdot x$  and  $y(x + 0.3)$ , where  $y$  is the calculated reduction factor. To get the true shape of the curve, therefore, rectangles of width  $0.3y$  were constructed at various points of the curve, and the curve  $b$  drawn graphically so as to have the same integral as the rectangles over their width.

It was found that the steep part of the curve between the maximum and the end was practically a straight line, and the point where this straight line cuts the range axis was taken as the end of the range. The ranges measured in this way were found to be at  $15^\circ$  C. and 76 cm. Hg.:—polonium 3.77 cm., actinium C 5.40 cm., radium C 6.92 cm., and thorium C<sub>2</sub> 8.60 cm., in good agreement with the values generally accepted\*. To make a comparison of the curves for the different products the distances were measured from the ends of the ranges and the ionization expressed as percentages of the maxima. In this way the curves given in fig. 6 were deduced.

Fig. 6.



It will be at once observed from an inspection of the figure that the different curves are not superposable; for instance,

\* Rutherford, 'Radioactive Substances,' p. 668.

the distance between the maximum and the end of the range is least for polonium and greatest for thorium  $C_2$ . This has apparently not been observed previously, though it is to be anticipated theoretically. It is known from experiments on the magnetic deflexion of  $\alpha$  particles that an initially homogeneous beam becomes slightly less homogeneous as absorption proceeds\*. This phenomenon was first predicted by Darwin† and termed by him "straggling." It is due to the fact that some  $\alpha$  particles suffer more severe encounters with the atoms of matter traversed than others. Consider a pencil of  $\alpha$  particles from thorium  $C_2$  which have traversed a distance from the source in air of  $8.6 - 3.77 = 4.83$  cm. These  $\alpha$  particles will have the same residual range, 3.77 cm., and consequently the same average velocity as a pencil of  $\alpha$  particles at the moment of their projection from atoms of polonium. Yet whereas in the latter case the velocities of every  $\alpha$  particle in the beam will be exactly the same, in the former case the velocities will have values grouped round the average, and in general differing from it by small amounts. It is easy to see that the ionization curve will be different in the two cases, and that the "knee" will be more pronounced in the case of polonium  $\alpha$  particles in agreement with the results shown in fig. 6.

As the  $\alpha$  particles of actinium C and radium C have ranges intermediate between those of thorium  $C_2$  and polonium, it is to be expected that the curves should show intermediate characteristics. Our results are in general agreement with this expectation. The experimental curves are, however, almost identical; whereas theoretically the actinium curve should be nearer to that for polonium, since the range of the  $\alpha$  particles of actinium C is smaller than the range of the  $\alpha$  particles of radium C. It must be remembered, however, that owing to the rapid decay of the active deposits of actinium and radium, the experimental error is somewhat increased and is probably greater than any deviation from what is to be anticipated theoretically.

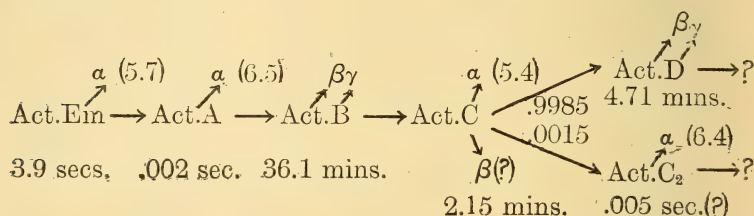
A comparison of figs. 3 and 6 will show that our measurements do not agree with those of Mlle. Blanquies, and that no definite evidence of further anomaly in the  $\alpha$  particles of actinium C, than those indicated in the first section of this paper, has been established.

\* Marsden & Taylor, *Proc. Roy. Soc. A.* lxxxviii. p. 443 (1913).

† Darwin, *Phil. Mag.* xxiii. p. 901 (1912). Cf. Marsden & Richardson, *Phil. Mag.* xxv. p. 184 (1913); also Bianu, *Le Radium*, x. p. 122 (1913).

*Scheme of Transformation.*

By analogy with the transformations in the active deposits of thorium and radium, the actinium active deposit may be written as follows:—



*i. e.* we may suppose that .9985 of the atoms of actinium C emit  $\alpha$  particles of range 5.4 cm. and become transformed into atoms of actinium D, while the other .0015 may be supposed to emit  $\beta$  rays and produce the new product  $C_2$ , whose period, assuming Geiger's formula to be applicable, ought to be about 1/200 second.

On such an hypothesis, actinium C ( $= C_1 + C_2$ ) may be presumed to emit practically no  $\beta$  radiation compared with actinium D. Experiments were made to test this point. Pure actinium C, without B or D, was deposited on nickel from hot acid solution, and the subsequent variation of activity measured by  $\beta$  rays. The curve rose from zero, showing initially that no detectable  $\beta$  radiation was present compared with that due to actinium D.

It is of interest to compare the characteristics of the products of the three active deposits, for they appear so analogous that such a comparison might throw light on the process occurring during disintegration. From the theory of the structure of the atom originally put forward by Prof. Sir E. Rutherford\*, it is probable that both  $\alpha$  and  $\beta$  rays originate in the central positive nucleus, while  $\gamma$  rays are a secondary effect due to the arrangement of the electrons. It thus appears probable that the ultimate cause of disintegration is connected with the structure of the nucleus rather than that of the atom as a whole, so that a study of radioactive transformation is one possible method of obtaining information on the properties of the nucleus. From the fact that the radiations emitted follow practically the same order in the three radioactive families, it would appear that the

\* Cf. Bohr, Phil. Mag. xxvi. p. 501 (1913). Rutherford & Robinson, Phil. Mag. xxvi. p. 728 (1913). Rutherford, Phil. Mag. xxvii. p. 488 (1914).

nuclei of corresponding products must have some fundamental characteristic in common.

In the following table the disintegration constants and properties of the products following the emanations are given, the numbers in the same row belonging to the family given in the first column. The  $\alpha$  rays are characterized by their ranges in air at 15° C. and 76 cm. Hg, and the  $\beta$  and  $\gamma$  rays by their respective absorption coefficients in aluminium, the numbers for  $\gamma$  rays being taken from the tables of Rutherford and Richardson\*. For theoretical purposes and for the establishment of empirical formulæ it would, no doubt, be better to give the velocities of the  $\alpha$  and  $\beta$  particles and the actual wave-lengths of the various  $\gamma$  rays, but such data are not yet complete and the numbers given are sufficient for qualitative comparisons. In the columns for  $C_\alpha$  and  $C_\beta$  are given the data for those atoms of the C products which emit  $\alpha$  and  $\beta$  rays respectively, and the chances of disintegration in any second in these two directions are denoted by  $\lambda_\alpha$  and  $\lambda_\beta$ †, where  $\lambda_\alpha + \lambda_\beta = \lambda_c$  ( $\lambda_c$  = the ordinary disintegration constant of C) and  $\lambda_\alpha/\lambda_\beta$  is the ratio of the numbers of atoms which are transformed in the two ways. It is obvious that the D products of actinium and thorium correspond to radium  $C_2$ , and the data for these products has therefore been placed in the same column, and similarly for the other corresponding products. When the schemes of transformation are fully investigated, a change of nomenclature will be advisable.

It will be noticed that in almost every column the thorium product lies intermediate in its characteristics between the corresponding products of radium and actinium. No direct information is at present available as to whether this is also the order of the atomic weights‡. An exception occurs in the B products, the transformation constants and the absorption coefficients of the hardest  $\gamma$  rays both following the order  $Ra > Act > Th$ . On the supposition mentioned above, this would apparently show that whatever irregularity there is in the nucleus of one of the products, it must also extend to one of the innermost rings of electrons. This question cannot be settled definitely, however, until the wave-lengths of the  $\gamma$  rays are known. Another exception is that the ranges of the particles of the  $C_2$  products (=  $Ra''$ ) follow the order  $Th > Ra > Act$ . In fact Swinne§, using

\* Rutherford & Richardson, *Phil. Mag.* xxvi. p. 938 (1913).

† Marsden & Darwin *loc. cit.*

‡ Cf. Fajans, *Phys. Zeit.* xiv. p. 5 (1913).

§ Swinne, *Phys. Zeit.* xiv. p. 142 (1913).



TABLE I.

Product:—	Emanation.		A.		B.		
	$\lambda(\text{sec.}^{-1})$ .	Range <sub>a</sub> .	$\lambda$ .	Range <sub>a</sub> .	$\lambda$ .	$\mu\beta$ .	$\mu\gamma$ .
Radium .....	$2.085 \times 10^{-6}$	4.16	$3.85 \times 10^{-3}$	4.75	$4.33 \times 10^{-4}$	13 91	230 40 0.51
Thorium.....	$1.28 \times 10^{-2}$	5.0	4.95	5.7	$1.82 \times 10^{-5}$	110	160 32 0.36
Actinium ...	$1.8 \times 10^{-1}$	5.7	350	6.5	$3.18 \times 10^{-4}$	very soft.	120 30 0.45

Product:—	C <sub>a</sub> .		C <sub>β</sub> .			C <sub>2</sub> (RaC').	D (RaC <sub>2</sub> ).		
	$\lambda_a$ .	Range <sub>a</sub> .	$\lambda_\beta$ .	$\mu_\beta$ .	$\mu_\gamma$ .	Range <sub>a</sub> .	$\lambda$ .	$\mu_\beta$ .	$\mu_\gamma$ .
Radium .....	$1.8 \times 10^{-7}$	?	$5.93 \times 10^{-4}$	13 53	0.115	6.94	$8.25 \times 10^{-3}$	13	?
Thorium ...	$6.7 \times 10^{-5}$	4.8	$1.23 \times 10^{-4}$	13.5	None.	8.60	$3.73 \times 10^{-3}$	21.5	0.096
Actinium ...	$5.4 \times 10^{-3}$	5.40	$8 \times 10^{-6}$	?	None.	6.4	$2.45 \times 10^{-3}$	28.5	0.198

empirical relations, predicted that, if actinium C<sub>2</sub> exists, it ought to have a range of 9.3 cm. and not 6.4 cm. as found in these experiments.

With regard to the supposed  $\alpha$  radiation of radium C<sub>a</sub>; these  $\alpha$  particles have not yet been observed owing to the very small number to be expected. In some experiments on the magnetic deflexion of  $\alpha$  particles by one of us, a search was made by assuming them to possess the velocity predicted by Geiger's formula for a period of 19.5 mins. The results were negative; but a fraction of less than about 0.005 of the main beam of  $\alpha$  particles would have escaped detection.

In view of the fact that the  $\beta$  radiations of thorium D and actinium D are much less penetrating than those of the  $C_\beta$  products, it is somewhat anomalous that the  $\beta$  rays of radium  $C_2$  (equivalent to Th D and Act D) have exactly the same penetrating power as those of radium  $C_{1\beta}$ . Again, although thorium C and actinium C emit no  $\gamma$  rays, yet radium C undoubtedly appears to ; for it is improbable that the relatively few atoms of radium  $C_2$  can give rise to the whole of the intense  $\gamma$  radiation of radium C. A closer examination of these latter points would be of interest.

In conclusion we wish to express our indebtedness to Prof. Sir E. Rutherford for his kind interest in this research.

LXXX. *The High-Frequency Spectra of the Elements.*

Part II. *By* H. G. J. MOSELEY, M.A.\*

THE first part † of this paper dealt with a method of photographing X-ray spectra, and included the spectra of a dozen elements. More than thirty other elements have now been investigated, and simple laws have been found which govern the results, and make it possible to predict with confidence the position of the principal lines in the spectrum of any element from aluminium to gold. The present contribution is a general preliminary survey, which claims neither to be complete nor very accurate.

A somewhat different method of photographing these spectra has been developed independently by de Broglie ‡ and by Herve §. The latter closely confirms the angles given by Moseley and Darwin || for reflexion of Pt rays from selenite. De Broglie finds less satisfactory agreement for the reflexion from rocksalt. De Broglie has also examined the spectra of W and Au, and has obtained for Cu and Fe results similar to those given in Part I.

The general experimental method has remained unaltered, and need not be again described. The same crystal of potassium ferrocyanide has been used as analyser throughout. The sharpness of the lines of short wave-length has

\* Communicated by the Author.

† Moseley, *Phil. Mag.* xxvi. p. 1024 (1913).

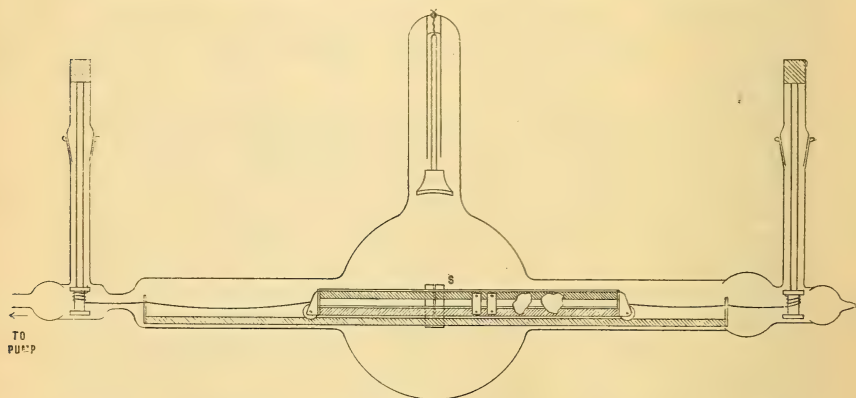
‡ De Broglie, *C. R.* 17 Nov., 22 Dec., 1913, 19 Jan., 2 Feb., 2 March, 1914.

§ Herve, *Verh. d. D. Phys. Ges.* xvi. p. 73, Jan. 1914.

|| Moseley & Darwin, *Phil. Mag.* xxvi. p. 210 (1913).

been much improved by reducing the breadth of the defining slit to about 0.2 mm. The most convenient type of X-ray tube is drawn to scale in fig. 1. The aluminium trolley which carries the targets can be drawn to and fro by means of silk fishing-line wound on brass bobbins. An iron screen S fastened to the rails is furnished with a fine vertical slit which defines the X-ray beam. The slit should be fixed exactly opposite the focus-spot of the cathode-stream, though a slight error can be remedied by deflecting the cathode rays with a magnet. The X rays escape by a side-tube  $2\frac{1}{2}$  cm. diameter closed by an aluminium window 0.022 mm. thick. The X-ray tube, which has a capacity of over 3 litres, was exhausted with a Gaede mercury-pump, for the loan of which I am indebted to Balliol College.

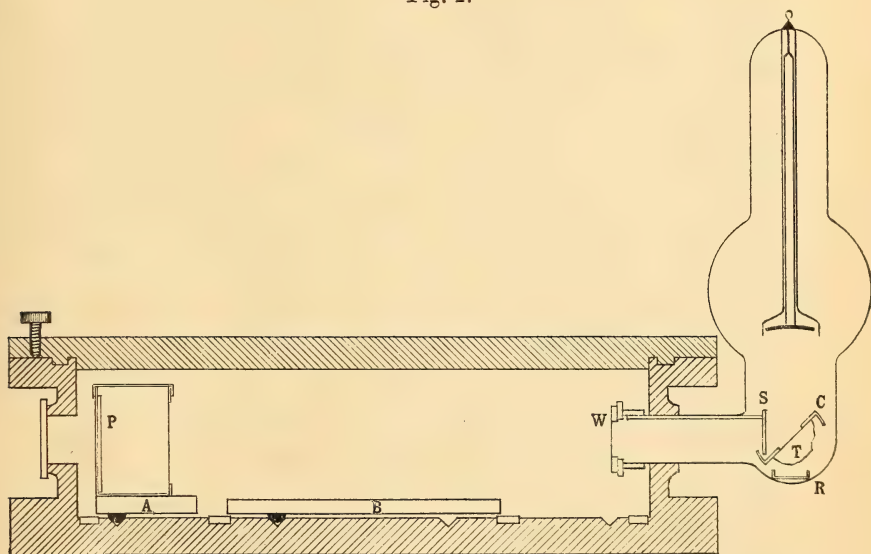
Fig. 1.



The radiations of long wave-length cannot penetrate an aluminium window or more than a centimetre or two of air. The photographs had therefore in this case to be taken inside an exhausted spectrometer. Fig. 2 gives a vertical section to scale of the X-ray tube and spectrometer. The former consists of a bulb containing the cathode, joined by a very large glass T-piece to a long tube of 4 cm. diameter, in which are the rails R and the carriage C. S is the defining-slit and W a window of goldbeaters' skin which separates the tube from the spectrometer. This material, which is usually air-tight, though sometimes it may require varnishing, is extremely transparent to X rays. A circular window of 2 cm. diameter will easily withstand the pressure of the atmosphere if left undisturbed. In these experiments, however, the pressure was relieved

every time the spectrometer was exhausted, and under such conditions the goldbeaters' skin had frequently to be renewed. The spectrometer, which was specially designed for this work, consists of a strong circular iron box of 30 cm. inside diameter and 8 cm. high, closed by a lid which, when the flange is greased, makes an air-tight joint. Two concentric grooves are cut in the floor of the box. The table A, which carries the plate-holder, rests on three steel balls, of which two run in the outer groove, while the third rests on the floor of the box. The position of the crystal-table B is controlled in like manner by the inner groove. This geometrical construction for a spectrometer is well

Fig. 2.



known. The scales are fixed to the box and the verniers to the tables. For these very soft rays the absorption by the black paper front of the plate-holder became serious, and two sheets of black tissue-paper were used instead. Lumps of the pure elements, usually several millimetres thick, were used as targets in the case of Mg, Al, Si, Mo, Ru, Pd, Ag, Sb, Ta. Foils such as Rh, W, Au were either silver-soldered or brazed onto copper. Os was used in the form of a thin chemical deposit on copper. The alloys used were ZrNi (70 per cent.), WFe (50 per cent.), NbTa (50 per cent.), and SnMn (50 per cent.). KCl and the oxides of the rare-earth elements were rubbed onto the surface of



nickel plates roughened with coarse emery-powder. The only serious difficulty in the experiments is caused by the heat produced by the cathode ray bombardment, and the consequent liberation of gas and destruction of the surface of the target. This makes it necessary to use the element in a form which is not too volatile and prevents the employment of a very powerful discharge. The total time of an exposure, including rests, varied from three minutes for a substance such as ruthenium, which could safely be heated, to thirty minutes for the rare earth oxides. The importance of using an efficient high-tension valve may again be mentioned.

The oxides of Sa, Eu, Gd, Er were given me by Sir William Crookes, O.M., to whom I wish to express my sincere gratitude. For the loan of the Os and a button of Ru I am indebted to Messrs. Johnson Matthey. The alloys were obtained from the Metallic Compositions Co., and the oxides of La, Ce, Pr, Nd, and Er from Dr. Schuchardt, of Görlitz.

Almost every line was photographed in two different orders, and the double angles of reflexion measured as before to within  $0^{\circ}1$  and sometimes  $0^{\circ}05$ . In some sets of experiments a small error caused by the crystal surface not being exactly on the spectrometer-axis gave rise to a systematic discrepancy in the results obtained from reflexion in different orders. It was found that this error, which never changed the reflexion-angle by more than  $0^{\circ}05$ , could be measured more accurately from the amount of the discrepancy than from direct observation of the crystal. A more serious correction was necessary when using the long wave-length apparatus. In this case the slit and photograph are not equidistant from the crystal, and the position of the spectrum-lines on the plate is no longer independent of the angle at which the crystal is set. The necessary corrections were calculated geometrically, and verified by photographing the same line for both right-handed and left-handed reflexions and with the crystal set at various angles.

In the work on the very short wave-lengths, the reflexion of the general heterogeneous radiation gave some trouble. This is always an important part of the radiation from an X-ray tube, but with a hard tube it is analysed by reflexion mainly into constituents of very short wave-length, and so usually does not interfere with the line-spectra. It is only with an extremely soft tube, combined with precautions against absorption by the air, that constituents reflected at large angles become prominent. When examining such a spectrum as that of Ag in the K series, the general reflexion

cannot be avoided. Unfortunately, when photographed it takes the form of irregular fringes, which effectually hide faint spectrum-lines. A change of target, with the position of slit and crystal unaltered, does not affect the appearance of the fringes, a fact which proves that they are due to the general heterogeneous radiation. It is easy to show that the fringes are merely a very foreshortened pattern of patches on the crystal surface which reflect exceptionally well. The way in which they move and spread out laterally as the crystal is turned provides a proof of this, and so does Barkla's \* observation that when the crystal is moved sideways the fringes move with it. It is easy to devise methods for getting rid of the fringes. In the first place, narrowing the slit or increasing the distance from the crystal will diminish their intensity compared with that of the line-spectrum. In the second place, turning the crystal will move and blur the fringes, but leave the sharpness of the lines unaffected provided the slit and photograph are equidistant from the reflecting surface †. The quantitative measurements of Moseley and Darwin ‡ on the reflexion of the general radiation must have been little affected by these fringes, as the incident beam was restricted to a very narrow pencil which always impinged on the same part of the crystal.

The results obtained for radiations belonging to Barkla's K series are given in Table I., and for convenience the figures already given in Part I. are included. The wave-length  $\lambda$  has been calculated from the glancing angle of reflexion  $\theta$  by means of the relation  $n\lambda = 2d \sin \theta$ , where  $d$  has been taken to be  $8.454 \times 10^{-8}$  cm. As before, the strongest line is called  $\alpha$  and the next line  $\beta$ . The square root of the frequency of each line is plotted in fig. 3, and the wave-lengths can be read off with the help of the scale at the top of the diagram.

The spectrum of Al was photographed in the first order only. The very light elements give several other fainter lines, which have not yet been fully investigated, while the results for Mg and Na are quite complicated, and apparently depart from the simple relations which connect the spectra of the other elements. In the spectra from yttrium onwards only the  $\alpha$  line has so far been measured, and further results in these directions will be given in a later paper. The

\* Barkla and Martyn, Proc. Phys. Soc. London (1913).

† Moseley, *loc. cit.* p. 1025. See also W. H. and W. L. Bragg, Proc. Roy. Soc. A, lxxxviii, p. 428 (1913).

‡ Moseley and Darwin, *loc. cit.*

TABLE I.

	$\alpha$ line. $\lambda \times 10^8$ cm.	QK.	N. Atomic Number.	$\beta$ line. $\lambda \times 10^8$ .
Aluminium .....	8.364	12.05	<b>13</b>	7.912
Silicon .....	7.142	13.04	14	6.729
Chlorine .....	4.750	16.00	17	.....
Potassium .....	3.759	17.98	19	3.463
Calcium .....	3.368	19.00	20	3.094
Titanium .....	2.758	20.99	22	2.524
Vanadium .....	2.519	21.96	23	2.297
Chromium .....	2.301	22.98	24	2.093
Manganese .....	2.111	23.99	25	1.818
Iron .....	1.946	24.99	26	1.765
Cobalt .....	1.798	26.00	27	1.629
Nickel .....	1.662	27.04	28	1.506
Copper .....	1.549	28.01	29	1.402
Zinc .....	1.445	29.01	30	1.306
Yttrium .....	0.838	38.1	39	.....
Zirconium .....	0.794	39.1	40	.....
Niobium .....	0.750	40.2	41	.....
Molybdenum .....	0.721	41.2	42	.....
Ruthenium .....	0.638	43.6	44	.....
Palladium .....	0.584	45.6	46	.....
Silver .....	0.560	46.6	47	.....

spectra both of K and of Cl were obtained by means of a target of KCl, but it is very improbable that the observed lines have been attributed to the wrong elements. The  $\alpha$  line for elements from Y onwards appeared to consist of a very close doublet, an effect previously observed by Bragg\* in the case of rhodium.

The results obtained for the spectra of the L series are given in Table II. and plotted in fig. 3. These spectra contain five lines,  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\epsilon$ , reckoned in order of decreasing wave-length and decreasing intensity. There is also always a faint companion  $\alpha'$  on the long wave-length side of  $\alpha$ , a rather faint line  $\phi$  between  $\beta$  and  $\gamma$  for the rare earth elements at least, and a number of very faint lines of wave-length greater than  $\alpha$ . Of these,  $\alpha$ ,  $\beta$ ,  $\phi$ , and  $\gamma$  have been systematically measured with the object of finding out how the spectrum alters from one element to another. The fact that often values are not given for all these lines merely indicates the incompleteness of the work. The spectra, so far as they have been examined, are so entirely similar that without doubt  $\alpha$ ,  $\beta$ , and  $\gamma$  at least always exist. Often  $\gamma$  was

\* Bragg, 'Nature,' March 12, 1914.

Fig. 3.

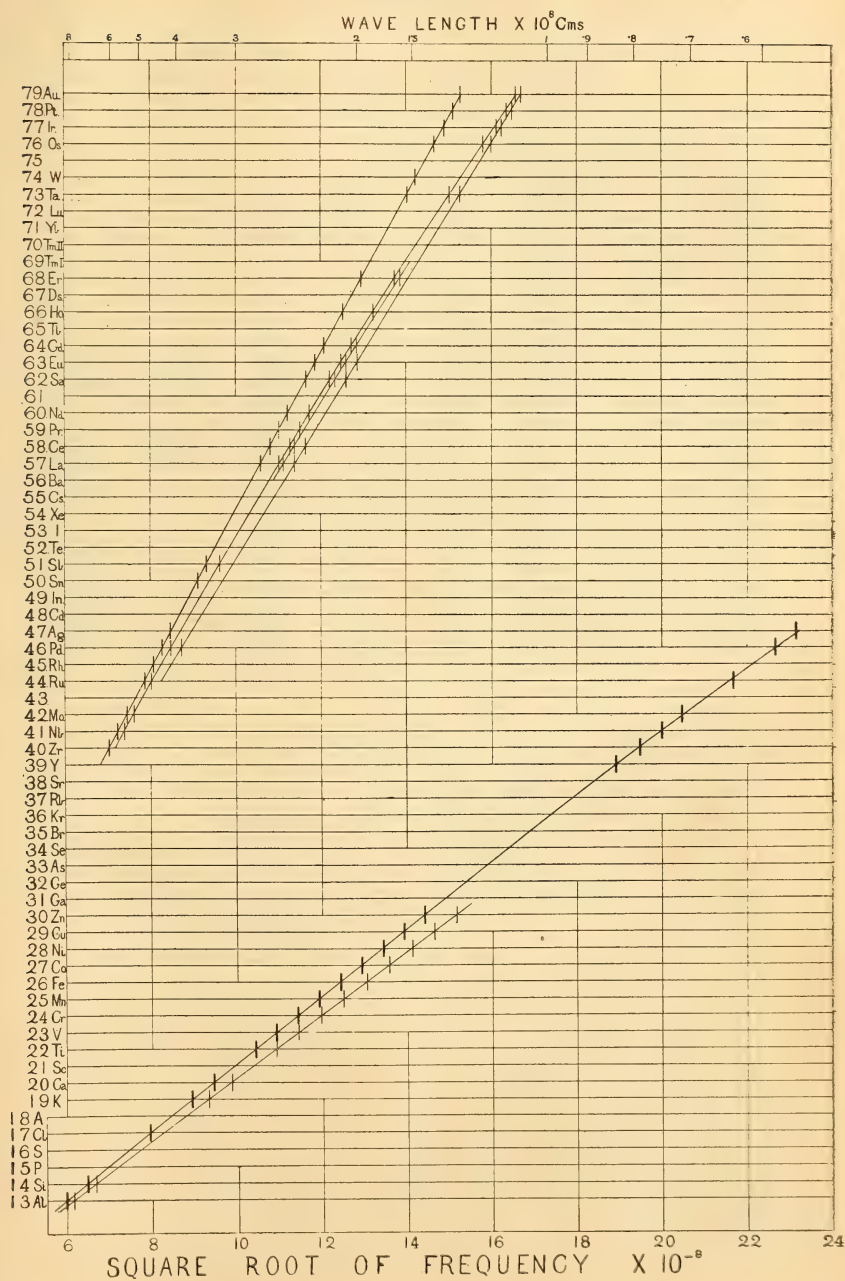




TABLE II.

	$\alpha$ line. $\lambda \times 10^3$ cm.	$Q_L$	N. Atomic Number.	$\beta$ line. $\lambda \times 10^3$ .	$\phi$ line. $\lambda \times 10^3$ .	$\gamma$ line. $\lambda \times 10^3$ .
Zirconium .....	6.091	32.8	40	.....	.....	.....
Niobium .....	5.749	33.8	41	5.507	.....	.....
Molybdenum.....	5.423	34.8	42	5.187	.....	.....
Ruthenium .....	4.861	36.7	44	4.660	.....	.....
Rhodium .....	4.622	37.7	45	.....	.....	.....
Palladium .....	4.385	38.7	46	4.168	.....	3.928
Silver .....	4.170	39.6	47	.....	.....	.....
Tin .....	3.619	42.6	50	.....	.....	.....
Antimony .....	3.458	43.6	51	3.245	.....	.....
Lanthanum .....	2.676	49.5	57	2.471	2.424	2.313
Cerium .....	2.567	50.6	58	2.360	2.315	2.209
Praseodymium ..	(2.471)	51.5	59	2.265	.....	.....
Neodymium .....	2.382	52.5	60	2.175	.....	.....
Samarium .....	2.208	54.5	62	2.008	1.972	1.893
Europium .....	2.130	55.5	63	1.925	1.888	1.814
Gadolinium .....	2.057	56.5	64	1.853	1.818	.....
Holmium .....	1.914	58.6	66	1.711	.....	.....
Erbium .....	1.790	60.6	68	1.591	1.563	.....
Tantalum .....	1.525	65.6	73	1.330	.....	1.287
Tungsten .....	1.486	66.5	74	.....	.....	.....
Osmium .....	1.397	68.5	76	1.201	.....	1.172
Iridium .....	1.354	69.6	77	1.155	.....	1.138
Platinum .....	1.316	70.6	78	1.121	.....	1.104
Gold .....	1.287	71.4	79	1.092	.....	1.078

not included in the limited range of wave-lengths which can be photographed on one plate. Sometimes lines have not been measured, either on account of faintness or of the confusing proximity of lines due to impurities.

Lines due to impurities were frequently present, but caused little trouble except in the rare earth group. Here two extreme cases occurred. The X-ray spectrum of the praseodymia showed that it consisted roughly of 50 per cent. La, 35 per cent. Ce, and 15 per cent. Pr. Unfortunately the position expected for the  $\alpha$  line of Pr coincides with the known position of the  $\beta$  line of La, but the  $\beta$  line of Pr was quite conspicuous, and had precisely the wave-length anticipated. Two specimens of erbia were used. The specimen purchased contained 50 per cent. Er and 50 per cent. of another element, of which the X-ray spectrum coincides with the spectrum calculated for Ho. The erbia given by Sir William Crookes was evidently nearly pure, but showed the  $\alpha$  and  $\beta$  lines of Ho quite faintly, and also faint lines agreeing with  $\alpha$  and  $\beta$  of Ds and  $\alpha$  of Tm I and of Tm II. The Nd was free from La, Ce, and Pr, but contained a fair

proportion of Sm. The Sm, Eu, and Gd appeared to be pure. I hope soon to complete the examination of the spectra of this group.

### Conclusions.

In fig. 3 the spectra of the elements are arranged on horizontal lines spaced at equal distances. The order chosen for the elements is the order of the atomic weights, except in the cases of A, Co, and Te, where this clashes with the order of the chemical properties. Vacant lines have been left for an element between Mo and Ru, an element between Nd and Sa, and an element between W and Os, none of which are yet known, while Tm, which Welsbach has separated into two constituents, is given two lines. This is equivalent to assigning to successive elements a series of successive characteristic integers. On this principle the integer  $N$  for Al, the thirteenth element, has been taken to be 13, and the values of  $N$  then assumed by the other elements are given on the left-hand side of fig. 3. This proceeding is justified by the fact that it introduces perfect regularity into the X-ray spectra. Examination of fig. 3 shows that the values of  $\nu^{\frac{1}{3}}$  for all the lines examined both in the K and the L series now fall on regular curves which approximate to straight lines. The same thing is shown more clearly by comparing the values of  $N$  in Table I. with those of

$$Q_K = \sqrt{\frac{\nu}{\frac{3}{4}\nu_0}},$$

$\nu$  being the frequency of the  $\alpha$  line and  $\nu_0$  the fundamental Rydberg frequency. It is here plain that  $Q_K = N - 1$  very approximately, except for the radiations of very short wavelength which gradually diverge from this relation. Again, in Table II. a comparison of  $N$  with

$$Q_L = \sqrt{\frac{\nu}{\frac{5}{36}\nu_0}},$$

where  $\nu$  is the frequency of the L  $\alpha$  line, shows that  $Q_L = N - 7.4$  approximately, although a systematic deviation clearly shows that the relation is not accurately linear in this case.

Now if either the elements were not characterized by these integers, or any mistake had been made in the order chosen or in the number of places left for unknown elements, these

\* Welsbach, *Monatsh.* xxxii. p. 373 (1911).

regularities would at once disappear. We can therefore conclude from the evidence of the X-ray spectra alone, without using any theory of atomic structure, that these integers are really characteristic of the elements. Further, as it is improbable that two different stable elements should have the same integer, three, and only three, more elements are likely to exist between Al and Au. As the X-ray spectra of these elements can be confidently predicted, they should not be difficult to find. The examination of keltium\* would be of exceptional interest, as no place has been assigned to this element.

Now Rutherford† has proved that the most important constituent of an atom is its central positively charged nucleus, and van den Broek‡ has put forward the view that the charge carried by this nucleus is in all cases an integral multiple of the charge on the hydrogen nucleus. There is every reason to suppose that the integer which controls the X-ray spectrum is the same as the number of electrical units in the nucleus, and these experiments therefore give the strongest possible support to the hypothesis of van den Broek. Soddy§ has pointed out that the chemical properties of the radio-elements are strong evidence that this hypothesis is true for the elements from thallium to uranium, so that its general validity would now seem to be established.

From the approximate linear relation between  $\nu^{\frac{1}{2}}$  and  $N$  for each line we obtain the general equation

$$\nu = A (N - b)^2,$$

where  $A$  and  $b$  are constants characteristic of each line. For the K  $\alpha$  line

$$A = \left( \frac{1}{1^2} - \frac{1}{2^2} \right) \nu_0 \quad \text{and} \quad b = 1.$$

For the L  $\alpha$  line approximately

$$A = \left( \frac{1}{2^2} - \frac{1}{3^2} \right) \nu_0 \quad \text{and} \quad b = 7.4.$$

The fact that the numbers and arrangement of the lines in the K and the L spectra are quite different, strongly suggests that they come from distinct vibrating systems, while the fact that  $b$  is much larger for the L lines than for the K lines

\* Urbain, *C.R. clii.* p. 141 (1911).

† Rutherford, *Phil. Mag.* xxi. p. 669 (1911), and xxvii. p. 488 (1914).

‡ Van den Broek, *Phys. Zeit.* xiv. p. 32 (1913), and 'Nature,' Nov. 27, Dec. 25, 1913, March 5, 1914.

§ Soddy, *Jahrbuch Rad. und. Elect.* x. p. 193 (1913); 'Nature,' Dec. 4, Dec. 18 (1913).

suggests that the L system is situated the further from the nucleus.

It was shown in Part I. \* that the linear relation between  $\nu^{\frac{1}{2}}$  and  $N-b$  was most naturally explained if the vibrating system was a ring of electrons rotating round the central nucleus with an angular momentum which was the same for the different elements. This view has been analysed and put in a more generalised form in a letter to 'Nature'†, written in answer to criticisms made by Lindemann‡.

*Summary.*

1. Every element from aluminium to gold is characterized by an integer  $N$  which determines its X-ray spectrum. Every detail in the spectrum of an element can therefore be predicted from the spectra of its neighbours.
2. This integer  $N$ , the atomic number of the element, is identified with the number of positive units of electricity contained in the atomic nucleus.
3. The atomic numbers for all elements from Al to Au have been tabulated on the assumption that  $N$  for Al is 13.
4. The order of the atomic numbers is the same as that of the atomic weights, except where the latter disagrees with the order of the chemical properties.
5. Known elements correspond with all the numbers between 13 and 79 except three. There are here three possible elements still undiscovered.
6. The frequency of any line in the X-ray spectrum is approximately proportional to  $A(N-b)^2$ , where  $A$  and  $b$  are constants.

I wish to thank Prof. J. S. Townsend, F.R.S., for providing me with every facility for carrying on this work, which has been greatly assisted by a grant from the Institut International de Physique Solvay.

Electrical Laboratory,  
Oxford.

\* *Loc. cit.* p. 1032.

† Moseley, 'Nature,' Jan. 15 (1914).

‡ F. A. Lindemann, 'Nature,' Jan. 1, Feb. 5, 1914.



LXXXI. *On the Activity of freshly-formed Radium Emanation.*

By HORACE H. POOLE \*.

AS there is no very satisfactory theoretical explanation of the exponential law of radioactive decay, it is not unreasonable to suppose that variations from it might occur under certain conditions. For instance, as has been suggested by Dr. Joly, it is possible that the rate of decay and hence the activity of a body might be anomalous when the body is freshly formed so that its age is only a very small fraction of its average life. Accordingly an attempt has been made to compare the activity of radium emanation a few seconds old with that of the same body at the age of a few minutes. If the exponential law holds the activities should be the same, as the decrease in the total quantity of emanation during the interval would be negligible.

The continuous flow method was employed. An air blast from a Roots blower was passed successively through a gas meter, a pressure regulator, and a drying-tube; it then passed over a thin film of impure radium chloride formed by evaporation on the upper surface of a small platinum ribbon, similar to that used in the Apophorometer, which was maintained at a white heat by means of an electric current. Thence the air current passed through a long plug of cotton wool, and after traversing a cooling tube entered the first testing vessel, from which it passed through a long wide lead pipe before entering the second testing vessel, which was exactly similar to the first in all respects. After leaving this the current was discharged in the open air by means of a tube leading out the window. Knowing the volume of air passing per second and the volumes of the various parts of the apparatus, it was easy to calculate the average age of the emanation entering the two testing vessels on the assumption that the emanation was liberated from the white hot strip as soon as formed. This seems to be the most doubtful point connected with the experiment, but it would seem probable that, as the strip was only slightly below the melting point of platinum, and the film of radioactive matter very thin, a very large percentage of the emanation must have been liberated within a few seconds of its formation.

In order to avoid trouble with the growth of active deposit in the testing vessels the air current was allowed to flow steadily over the heated strip for at least three hours before readings were taken, so that the active deposit might attain equilibrium with the emanation passing through. During

\* Communicated by the Author.

this period the testing vessels were kept charged, the central wires being earthed so as not to cause variations in the distribution of the deposit. Before the commencement of an experiment the strip was thoroughly deemanated by heating, the emanation which had accumulated on it being swept away down a pipe leading out the window.

The testing vessels were copper cylinders about 3.2 cm. in diameter and 180 c.c. volume mounted vertically side by side. They were connected together and charged to a negative potential of 143 volts by means of a battery of small dry cells. The central wires of the testing vessels passed through earthed guard tubes in the rubber stoppers which closed the upper ends of the vessels, being insulated from the guard tubes by means of sulphur. Either of these wires could be connected to the electrometer or earthed by means of two small mercury cups inside an earthed metal vessel fixed just above the testing vessels. Except when connected to the isolated quadrant of the electrometer during a test, the wires were always earthed. The air current entered the vessels by side tubes near the top, and left them by vertical tubes in the centre of the conical bottoms. The inlet tubes were tangential so that the air current would flow down the vessels in a helical path instead of forming irregular eddies.

A Dolezalek electrometer was used with a fairly coarse quartz suspension such that the deflexion per volt was about 160 scale-divisions, the needle being charged to a potential of 143 volts. The earthing key consisted of an iron wire dipping into the mercury cup used for connecting the testing vessels.

As it was necessary to prevent active deposit and also ions formed during the passage of the emanation through the long tube from entering the second testing vessel, this was guarded by a second cotton-wool plug. It was also necessary that the air in the two testing vessels should be at approximately the same temperature as otherwise the emanation would traverse the two at unequal rates. Accordingly, between the cotton-wool plugs and the testing vessels, the air flowed through two straight brass tubes 38 cm. long placed side by side in the same water-jacket. Inside these tubes, which were 9.2 mm. internal diameter, were mounted two smaller tubes 6.45 mm. external diameter blocked at each end, so that the air current traversed the narrow annular space between the tubes, thus encountering a large cooling surface in a small volume. The inner tubes were insulated from the outer ones and charged to the same potential as the vessels, thus providing an electric field of about 1040 volts

per centimetre to remove any ions which might possibly have got through the plugs.

The testing vessels were interchanged to eliminate any difference in the vessels themselves. Their natural leak was found while passing a current of pure air at the same rate as the emanation carrying current. In most of the experiments this was about 20 c.c. per second.

Preliminary observations with a pair of testing vessels differing slightly from those described, indicated that the difference between the activities of radium emanation at ages of 10 seconds and 5 minutes was certainly small, and apparently zero. It was found necessary to keep the platinum strip at a bright white heat as otherwise, if its temperature were raised, there was a large temporary increase in the ionization currents through the vessels, indicating that accumulated emanation was being evolved. At this high temperature radioactive particles were apparently given off by the strip, and were deposited on the walls of the containing glass vessel and on the cotton-wool filter plug. Owing to the use of insufficient filters in the first experiments the testing vessels used became slightly radioactive and were accordingly discarded in favour of those described above. By the use of a sufficiently thick plug the radioactive dust was prevented from reaching the testing vessels, but it of course accumulated on the plug and on the walls of the vessel surrounding the incandescent strip, where it apparently gave off its emanation irregularly, thus causing variations in the ionization currents through the testing vessels and so limiting the accuracy attainable.

When determining the natural leak of the testing vessels the air current passed through the cotton-wool plug, but not, of course, through the vessel containing the strip, so that the natural activity included that due to emanation from any radium on the plug, but was not affected by radium on the walls of the vessel.

The ionization currents through the two vessels were measured alternately, the average rate of motion of the electrometer needle during a period of about ten minutes being determined for each vessel in turn. When this had been done two or three times for each vessel, the connexions of the vessels were changed so that the air current traversed the vessels in the reverse order. This was done without stopping the air current flowing over the incandescent strip. Its constancy was tested by timing the revolutions of the gas meter. More readings of the ionization currents were then taken.



The following is a typical set of results arranged in order. A is the average ionization current for about ten minutes through one testing vessel in scale divisions per minute, B that for the other vessel: the third column shows the order of sequence of the vessels as regards the air current.

A	B	AB
3·63		
	3·59	"
3·76		"
	3·60	"
	(3·47)	BA
(3·24)		"
	3·40	"
3·41		"
	3·77	"
3·98		"

The figures in brackets should, perhaps, be disregarded, as they were obtained very shortly after the reversal and so might be affected by irregularities due to the temporary stoppage of the emanation current through the vessels during the changing of the connexions. Taking means of the remaining figures, and subtracting the natural activities of the vessels, which were 0·51 for A and 0·44 for B, we obtain:—

A	B	AB
3·18	3·15	
3·18	3·14	BA

As these figures are only the means of the above results, which involve such large variations, little stress can be laid on their remarkable agreement beyond the fact that they show that it is improbable that the variation between the activities of the emanation in the first and second vessels exceeds 5 per cent., as such a difference would probably have been noticeable. Other determinations gave similar results; irregular fluctuations always occurred, the ionization currents sometimes increasing and sometimes decreasing, but the mean for the first and second vessels was always nearly the same.

In the determination to which the above figures apply the age of the emanation entering the first vessel was estimated at about 5 seconds on the hypothesis that no time was wasted in deemanation; the time required to traverse the vessel was about 9 seconds, making the average age of the emanation in the first vessel about 10 seconds. The age of the emanation in the second vessel was 5 minutes.

Other determinations were made with less rapid air  
*Phil. Mag. S. 6. Vol. 27. No. 160. April 1914.* 3 B



currents and the ionization currents found to be approximately inversely proportional to the rate of the air current, as they ought to be.

This point was being tested more accurately when the experiments were brought to an end by the melting of the platinum strip, and as it seemed unlikely that very much more information would be obtained the work was discontinued.

The chief uncertainty about the results is probably the question as to the time taken in emanation of the radium film. This being so there seemed to be little object in testing the activity of emanation whose average age was nominally less than 10 seconds, as might have been done by modifying the arrangement, since it is quite likely that several seconds are occupied in setting free the emanation.

The general result obtained is that the activity of radium emanation is the same within a few seconds of its formation as at some minutes later. A variation of 5 per cent. would probably have been detected. Thus no variation from the Exponential Law has been detected.

In conclusion I wish to thank Dr. Joly for his kind interest and valuable suggestions during the progress of this work.

Physical Laboratory,  
Trinity College, Dublin.

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LXXXII. *On a Classification of Foaming Solutions.* By  
S. A. SHORTER, D.Sc., Assistant Lecturer in Physics in  
the University of Leeds\*.

IN order for solutions to be capable of forming durable foam, the surface tension must be capable of local variations. It has been recognized for a long time that this power of local variation of the surface tension is due to the existence of a surface pellicle differing in composition from the interior portions of the liquid†.

Investigation of the properties of the surface layers of solutions has led me to the conclusion that though the above general explanation is true, there are important differences in the nature of the processes involved in the foaming of different solutions.

There are two distinct points to be considered with respect to the phenomenon of foaming. One is the nature of the

\* Communicated by the Author.

† See Rayleigh, *Scientific Papers*, vol. iii. p. 351.

process of formation of the surface layer. The other is the manner in which the surface layer contributes to the durability of the liquid film. It is upon differences with respect to these two points, that a classification of foaming solutions may be based.

The durability of thin films may be due to two causes:—  
 (1) the power of local variation of the surface tension, unaccompanied by any special superficial viscosity or rigidity,  
 (2) extreme viscosity or rigidity of the surface layers. Mixtures of acetic acid and water and soap solutions owe their foaming power to the first cause; aqueous solutions of albumin, saponin and peptone, to the second cause. Schütt\* has shown that the surface layers of a soap solution are devoid of any special viscous resistance to shear. I have shown† that even in the case of a fresh surface of a solution of saponin, there is a definite elastic resistance to shear, though the process of elastic relaxation makes the surface appear merely viscous when a steady shearing process is applied. Towards a transient stress such as would be caused by a slight disturbance, the surface layer would behave like an elastic substance.

We will next consider how the actual process of formation of the surface layer differs in different solutions. In a case such as that of a mixture of acetic acid and water, equilibrium between the surface layers and the body of the solution is attained rapidly (except in the case of very dilute solutions), so that the process of extension of the surface may be conducted in a thermodynamically reversible manner‡. In the case of solutions of soap and saponin, the process seems to be of a different nature. Milner§, from observations on solutions of sodium oleate, concludes that the process is an irreversible one. In the case of solutions of saponin, peptone and albumin, I have shown|| that the process of formation of the surface layer proceeds for several weeks without any sign of equilibrium. The substance forming the surface layer separates from the body of the solution at a rate practically independent of the thickness of the surface layer already formed. The process is thus thermodynamically irreversible. In the case of solutions of albumin the process seems to be also chemically irreversible, the film substance being insoluble in water¶.

\* *Ann. der Phys.* xiii. p. 712 (1904).

† *Phil. Mag.* xi. p. 317 (1906).

‡ See Donnan and Barker, *Roy. Soc. Proc. A.* lxxxv. p. 557 (1911).

§ *Phil. Mag.* xiii. p. 96 (1907). || *Phil. Mag.* xvii. p. 560 (1909).

¶ See Ramsden, *Roy. Soc. Proc.* lxxii. p. 156 (1903).

We have, therefore, three distinct classes of foaming solutions, having the following characteristics :—

- (1) Surface concentration thermodynamically reversible : special superficial viscosity or rigidity absent.
- (2) Surface concentration thermodynamically irreversible: special superficial viscosity or rigidity absent.
- (3) Surface concentration thermodynamically irreversible: the surface layers specially viscous or rigid.

Classes (2) and (3) might each be subdivided on the basis of the *chemical* reversibility of the process of surface concentration. At present, however, little seems to be known on this point\*.

This classification is evidently of fundamental importance, not merely in the study of foaming solutions, but also in relation to the phenomenon of surface concentration in general. Thus Lewis † has measured the "surface excess" at the interface between various solutions and a hydrocarbon oil, and found in many cases that the values obtained were of a different order of magnitude from those calculated from Gibbs's thermodynamical theory ‡. This discrepancy is explained by the fact that the solutions used did not belong to class (1), to which alone Gibbs's theory applies.

The University, Leeds,  
Sept. 18, 1913.

LXXXIII. *A Determination of the Periods of Transformation of Thorium and Actinium Emanation.* By P. B. PERKINS, Ph.D., *Honorary Research Fellow, University of Manchester*§.

RECENT investigations to determine the molecular weight of the thorium and actinium emanations presuppose an accurate knowledge of the half-value periods of these substances.

Owing to their rapid decay, especially that of the latter, ordinary electroscope methods of determining the decay constants cannot be used.

Debierne || first measured the period of decay of actinium

\* See Robertson, "The Proteins," University of California Publications in Physiology, vol. iii. No. 16 (1909).

† Phil. Mag. xvii. p. 466 (1909).

‡ Scientific Papers, vol. i. p. 235.

§ Communicated by Sir Ernest Rutherford, F.R.S.

|| Debierne, *C. R.* cxxxvi. p. 446 (1903).

emanation using the constant-flow method, and obtained a value 3.9 seconds. Two years later Hahn and Sackur\* found the value to be the same. In 1912 Miss Leslie†, using the direct method, found a mean value of 3.92 seconds, as a result of a large number of experiments, which, however, showed wide variations from the mean.

The earlier experiments of Rutherford‡ on thorium emanation gave a half-value period of about 60 seconds. Rossignol and Gimmingham§, by a similar method, lowered the value to 51 seconds. Hahn||, using the constant flow method, obtained 53.3 seconds. Bronson's¶ direct constant deflexion method gave a value of 54 seconds, and largely eliminated sources of error in the previous investigations. Miss Leslie's\*\* experiments gave values varying from 53.5 to 55.1, with a mean of 54.3 seconds.

Before attempting some work involving the square roots of these transformation periods, it seemed necessary if possible to determine them to one-half per cent.

Since the transformation constant of any radioactive substance is determined from the equation  $\lambda = \frac{\log_e I_0/I}{t}$ , where  $I_0$  is the initial activity, and  $I$  the activity after a time  $t$ , it is obvious that the relative error in  $\lambda$  is decreased as  $t$  is increased, provided  $I_0/I$  can be determined with the same degree of accuracy in each case. In practice the difficulty arises in obtaining  $I_0/I$  exactly when  $I$  is a very small fraction of  $I_0$ . In the present method this difficulty has been eliminated.

The rate of movement of the leaf of an electroscope varies inversely with the total capacity of the leaf system. If a large amount of a rapidly decaying gas be introduced into an electroscope, it is therefore possible to follow its decay by noting the rates of leak, when capacities diminishing in amount are successively connected in parallel with the leaf as decay proceeds. This device was used in the present investigation. The rates of deflexion were corrected for the growth of the active deposit and the ratios between the capacities were determined under experimental conditions.

\* Hahn and Sackur, *Chem. Ber.* xxxviii. p. 1943 (1905).

† Miss Leslie, *Phil. Mag.* xxiv. p. 637 (1912).

‡ Rutherford, *Phil. Mag.* xlix. p. 1 (1900).

§ Rossignol and Gimmingham, *Phil. Mag.* viii. p. 107 (1904).

|| Hahn, *Jahrbuch d. Radioakt.* ii. p. 233 (1905).

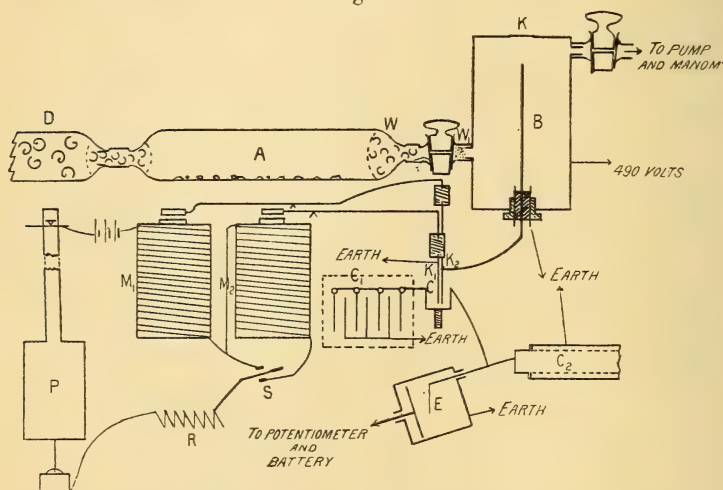
¶ Bronson, *Amer. Journ. Sci.* xix. p. 185 (1905).

\*\* *Loc. cit.*



The arrangement of the apparatus is shown in fig. 1. B is a cylinder into which the emanation was introduced. The

Fig. 1.



central electrode was connected to the electroscopical unit E, and to a series of capacities  $C_1$  and  $C_2$ . The chamber B, 8 cm. in diameter and 14 cm. high, was air-tight and provided with two stopcocks, one leading to the pump and manometer, the other to the source of emanation.

By slightly exhausting the chamber the emanation from radio-thorium or actinium, wrapped in filter-paper and enclosed in glass tubes placed at A, could be quickly swept into the chamber, by air entering through the drying-tube D. Plugs of cotton- and glass-wool W and  $W_1$ , respectively, were inserted to prevent "old" active deposit from entering the chamber along with the emanation. The electrode was about 2 mm. in diameter, and passing through an earthed guard-ring, reached to within 2 cm. of the top of the chamber, and was joined through an insulated brass cup C to the gold-leaf of a Wilson-Kaye electroscopical unit E. A thin copper window K permitted  $\beta$  rays to enter the chamber from a source above for standardization purposes. The chamber was insulated and joined through a water resistance to a battery of 490 volts. The capacity  $C_1$  was a standard mica condenser, divided into parts marked .1, .02, .005, and .001 microfarad respectively, and  $C_2$  was a small cylindrical capacity of approximately 470 cm. Keys  $K_1$  earth connected and  $K_2$  to which the

electrode leading into the ionization-chamber was joined, were controlled by small electromagnets  $M_1$  and  $M_2$ . The latter were energized at will by several storage-cells in series with a resistance  $R$ , a three-pole double-throw switch  $S$ , and a massive half-seconds pendulum  $P$  provided with a needle-point dipping into a mercury cup. When both keys  $K_1$  and  $K_2$  were down, the condensers, gold leaf, cup  $C$ , and electrode were earthed. With the switch  $S$  thrown into one position, the earthing key  $K_1$  was raised by the next contact of the pendulum and the gold leaf allowed to charge: in the other position of the switch the key  $K_2$  was raised, disconnecting the ionization-chamber from the gold leaf, thus permitting the deflexion of the gold leaf to be accurately determined. Small catches carried on upright brass strips supported the keys after being raised, and could be released at will by cords attached to them. The plate of the electroscope was joined through a water resistance and a potentiometer to a battery of 200 volts. By moving the arm of the potentiometer the sensibility of the electroscope could be adjusted. It varied in different experiments from 20 to 40 divisions per volt. Thick lead plates protected the chamber  $B$ , cup  $C$ , capacities and electroscope from the direct radiation of the active material used as source. A small sounder, placed in series with the pendulum circuit, rendered it easy to note the time at which the keys  $K_1$  and  $K_2$  were raised.

#### *Order of Experiment.*

The natural leaks with the various capacities in parallel with the electroscope were determined at the beginning of an experiment. In the case of actinium emanation the order of the experiment was as follows:—The capacity marked .1 m.f. was connected in parallel with the leaf, both keys  $K_1$  and  $K_2$  being earthed. The pressure in the chamber  $B$  was lowered usually about 2 or 3 cm., as recorded on the manometer, and the stopcock leading to the pump closed. The pendulum was set vibrating through a small arc and the counting of these vibrations begun, when the stopcock leading to the tube  $A$ , containing the emanation, was opened. This was closed after 3 or 4 seconds. Since the sounder and keys  $K_1$  and  $K_2$  were controlled by the beats of the pendulum, it was possible to record the exact time at which these keys were raised. When  $K_1$  was raised the deflexion of the gold leaf began, and after 2 seconds, *i.e.*, 4 beats, the key  $K_2$  was raised, thus disconnecting the chamber from the electroscope. The keys were then allowed to fall, and the total deflexion recorded. As decay proceeded, smaller and smaller capacities

were inserted and the times and deflexions for 4 beats were recorded. As practically all of the emanation had disappeared in 55 seconds, it required a certain amount of practice to take and record correctly from 5 to 7 readings in the time available. As the rate of production of the active deposit in the chamber during the decay of the emanation was so rapid, it was deemed advisable to obtain as many points on the decay curve as possible since, in taking the final readings with no auxiliary capacity in parallel with the leaf, a large percentage of the leak was due to the active deposit formed. After the last reading was taken, the vibrations of the pendulum were still counted until a given second on a chronometer was noted. The time of the beginning of the experiment was therefore known for making the necessary active deposit corrections. The growth of the active deposit was then observed until it reached a maximum, about 9 min. after the beginning of the experiment.

The same general order of experiment was used for thorium emanation. The rate of decay is so much slower for thorium emanation that the time at which the deflexions were read was taken from a chronometer. As before, deflexions were observed during a given number of vibrations of the pendulum, between the raising of the keys  $K_1$  and  $K_2$ . Ten or twelve beats, *i. e.* 5 or 6 seconds, was used in general. Readings extended over 12 or 13 minutes and the growth of the active deposit was observed for 30 minutes after the beginning of the experiment.

A study was made of the possibility of a residual charge existing in the mica condenser and thus influencing the succeeding readings, especially in the case of thorium emanation where charging occurred during 5 or 6 seconds. No residual effect could be observed under the experimental conditions used. If such an effect exists it must be very small as the capacity is charged from zero to a very small potential.

#### *Determination of the Capacity Ratios.*

The accuracy of this method depends largely on the degree of exactness with which the ratios, between the different capacities used, can be determined. These ratios were obtained a number of times during the investigation by observing the rates of leak due to a constant source of ionization when the various capacities were connected in the leaf system. Two methods were used :—(a) the  $\beta$  rays from a source of radium emanation were fired through the window K into the chamber, (b) the  $\alpha$  ray activity of radium emanation and its

products introduced into the chamber, was observed. Both methods gave the same values for these ratios. These relations were determined under the same experimental conditions as the decay of actinium emanation was observed. For a given capacity in parallel with the leaf its deflexion was noted for a certain number of vibrations of the pendulum, taking place between the raising of the keys  $K_1$  and  $K_2$ . For a larger or smaller capacity the number of vibrations was counted which gave about the same deflexion as before. The natural leaks were subtracted and the ratio calculated. This eliminated any variation in rates of deflexion at different parts of the scale. The scale was calibrated, however, for the sensitivities used and the necessary corrections made for readings over different parts when obtaining the periods of decay.

TABLE I.

Ratio.	Exp. Value.	Variation of individual determinations from mean.	Ratios of capacities with '1, '02, &c., in parallel with leaf to leaf, and connexions alone.
'1+electroscope, &c.	5.03	.6 per cent.	1361.0
'02+electroscope, &c.			
'02+electroscope, &c.	3.91	1.8 " "	270.6
'005+electroscope, &c.			
'005+electroscope, &c.	4.68	.8 " "	69.2
'001+electroscope, &c.			
'001+electroscope, &c.	1.70	1.0 " "	14.79
$C_2$ +electroscope, &c.			
$C_2$ +electroscope, &c.	8.70	1.0 " "	8.70
Electroscope, &c.			

The first column of Table I. gives the various ratios employed. The total capacity used at any time is the sum of the auxiliary capacity and that of the electroscope, cup C, chamber, leads, &c. Column II. shows the experimental ratios obtained. The degree of accuracy with which these values could be determined is stated in column III. The last column records the ratios of the various auxiliary capacities plus electroscope, leads, &c., to that of the electroscope, leads, &c., alone.

#### *Experimental Errors.*

Over the interval used in these experiments, *i. e.*, from 10 to 12 times the half-value periods, it can be easily calculated

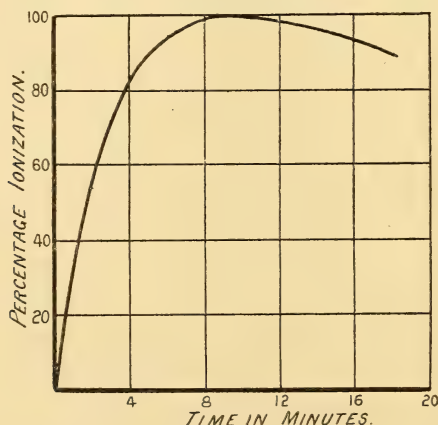


that an error of 10 per cent. in reading a deflexion during decay or in finding the capacity ratios would change the value of the decay period less than 1.5 per cent. The amount of emanation drawn into the chamber was so regulated that deflexions varying from 5 to 10 divisions were observed. Since the leaf was at rest when readings were made, it was possible to read to tenths with an error of not more than 1 or 2 per cent. The small percentage variations of the individual determinations of the capacity ratios given in Table I., show that the error made in obtaining these ratios could not appreciably affect the half-value periods.

#### *Corrections.*

In order to correct the observed readings for the activity produced in the chamber by the formation of the active deposit, the theoretical curves for the rise of activity of the C products were plotted\*. The larger part of the ionization obtained by the production of the active deposit is due to the  $\alpha$  particles from the C products, as the A products practically decay with the emanation. The  $\beta$  ray effect of the B products was also neglected.

Fig. 2.

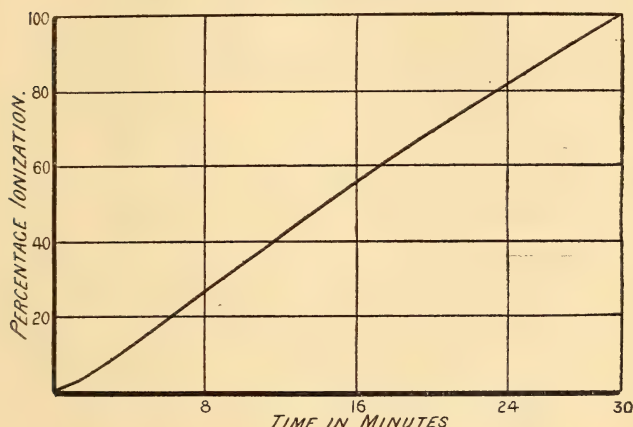


Figs. 2 and 3 show these curves for actinium and thorium respectively. In the case of actinium emanation the maximum activity was observed about 9 minutes from the beginning of the experiment, a result in agreement with the theoretical curves shown in figs. 2 and 3. The activity at

\* See Rutherford's 'Radioactive Substances,' p. 421 (1913).

that time was taken as 100 per cent. and corrections made corresponding to the time at which each deflexion was noted.

Fig. 3.



Since the growth of the active deposit of thorium was very much slower, the theoretical curve was plotted for a period of 30 minutes and the corrections made using the activity observed after 30 minutes as 100 per cent.

When studying the decay of actinium emanation, deflexions during 2 seconds were recorded. This time is rather long as compared with the half-value period. It would therefore appear that the average activity would not represent the true activity at the mean time, *i. e.*, 1 second from the beginning of deflexion. Calculation shows, however, that this correction factor only amounts to  $\cdot 9936$ , and is absolutely negligible for thorium emanation when deflexions extended over the time used.

The exact period of the pendulum, determined over a considerable time by a stop watch, was 1.005 seconds.

#### *Data and Results.*

The complete data for an experiment with actinium emanation are given in Table II.

The natural leak without auxiliary capacity in parallel with the electroscope was 5.1 divisions per minute.

In order to obtain an idea of the value of each experiment the log curves were plotted on a large scale. Points falling on or near the log curve, separated as far as possible in time,

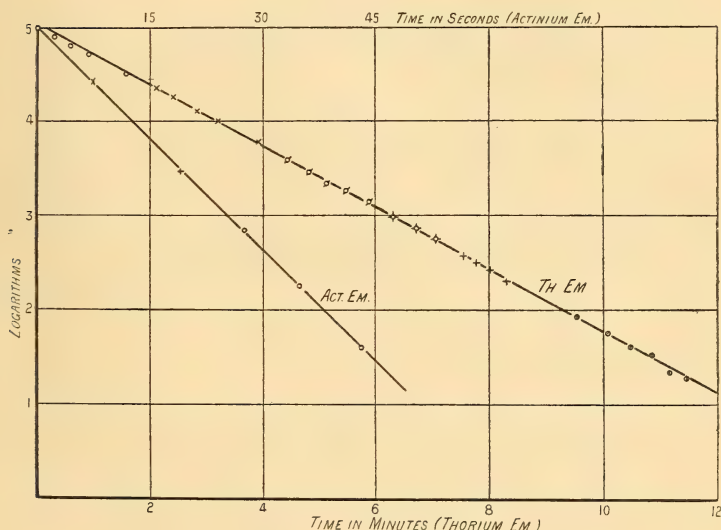
TABLE II.

Auxil. Cap.	Peud. Beats.	Time secs. from 1st.	Defl. (4 beats).	Corrected for scale calib.	Div. Min.	Decay correction. .9936.	Corrected for nat. leak.	Corrected for active deposit.	Cap. ratio.	Activity.	Log.
.02	13	0	9.7	9.7	286	284	284.0	284.0	270.6	100000	5.0000
.005	28	7.53	10.6	10.6	315	313	312.9	312.86	69.2	28170	4.4495
C <sub>2</sub>	51	19.07	10.6	10.6	315	313	312.4	311.1	8.70	3522	3.5467
0	68	27.61	21.1	20.4	603	600	594.9	580.6	1	755.5	2.8782
0	83	35.14	6.0	6.15	181.5	180.5	175.4	157.6	1	205.0	2.3119
0	99	43.17	2.0	2.05	58.5	58.2	53.1	31.7	1	41.25	1.6154
115th beat of pendulum at 4.0, 50.				Activity due to Act. Dep. 9 min. from start 89.1 $\frac{\text{div.}}{\text{min.}}$ .				Half-value period. Mean of three separate determinations = 3.92 secs.			

were then selected for initial and final values and substituted in the equation  $P = \frac{.6931t}{\log_e I_0/I}$ ,  $t$  being the time in seconds,  $I_0$  and  $I$  the initial and final activities, and  $P$  the half-value period.

Fig. 4 shows the log. curve from data given in Table II., as well as one for an experiment with thorium emanation,

Fig. 4.



giving a calculated half-value period of 54.6 seconds as the mean of three separate determinations.

Table III. contains the results from a number of experiments with actinium and thorium emanation. These give mean values for the half-value periods of 3.92 and 54.53 seconds respectively, corresponding to  $\lambda = .1768$  and  $.01271$  respectively.

### Resumé.

By successively inserting suitable capacities in parallel with the leaf of a Wilson-Kaye electroscope as decay progressed, the half-value periods of thorium and actinium emanation were found to be  $54.53 \pm .041$  and  $3.92 \pm .004$  respectively.



TABLE III.

ACTINIUM EMANATION.						THORIUM EMANATION.					
No. of Exp.	Initial activity.	Final activity.	Correct time in secs.	Calc. period.	Mean period.	No. of Exp.	Initial activity.	Final activity.	Correct time in secs.	Calc. period.	Mean period.
1 {	107800	814.5	27.60	3.92	3.92	1 {	23390	39.30	504.0	54.5	54.65
2 {	107800	221.1	35.15	3.94	3.94	2 {	23390	19.33	561.6	54.8	54.40
3 {	30380	221.1	27.60	3.89	3.89	3 {	8900	141.40	325.0	54.7	54.76
4 {	107800	506.3	30.60	—	3.95	4 {	38400	82.18	485.0	54.9	54.45
5 {	107800	693.1	28.60	3.93	3.89	5 {	38400	25.17	581.0	54.7	54.50
6 {	27830	146.1	29.10	3.84	3.94	6 {	19560	65.65	450.0	54.9	54.75
7 {	24530	506.3	22.10	—	3.92	7 {	17550	278.00	328.2	54.7	54.45
8 {	31920	1554.0	17.10	—	3.92	8 {	10380	278.00	280.8	53.8	54.50
9 {	107800	966.0	39.70	—	3.93	9 {	7350	168.00	29.7	—	54.20
10 {	33600	337.8	25.62	3.86	3.89	10 {	14880	20.80	514.0	—	54.75
11 {	114200	157.4	37.18	3.91	3.95	11 {	33050	11.35	632.0	54.9	54.45
12 {	107800	763.7	28.10	—	3.91	12 {	8060	11.35	515.0	54.6	54.65
	104300	2270.0	21.60	—	3.91		64300	19.50	646.0	55.3	
	107800	384.6	31.65	3.90	3.91		64300	38.60	592.0	53.6	
	34620	183.8	29.62	3.92	3.91		24700	36.10	514.0	54.7	
	107800	456.5	30.63	3.89	3.90		15300	30.70	489.0	54.6	
	30200	41.62	37.18	3.91	3.90						
General Mean = 3.92 ± .004.						General Mean = 54.53 ± .041.					

*Conclusion.*

In conclusion I wish to acknowledge the assistance of Mrs. Perkins in making the capacity adjustments and recording the beat of the pendulum at which deflexions began for actinium emanation, also to express my indebtedness to Prof. Sir Ernest Rutherford for his continued interest in the progress of the investigation, and to Mr. Marsden for many helpful suggestions.

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LXXXIV. *On the Effect of a Magnetic Field on Metallic Resistance.* By WALTER A. JENKINS, M.Sc., 1851 Exhibitioner, Research Student of Emmanuel College, Cambridge\*.

[Plate X.]

THE following experiments were carried out in order to obtain further evidence on the above effect. Nickel was the metal used, as the author had previously carried out experiments on the elongation of nickel under a longitudinal magnetic field and, as will appear later, in all probability there is some relation between the two effects.

*Apparatus.*

The nickel resistance consisted of a short piece of very fine wire soldered at right angles to the ends of two thick copper wires. The copper wires fitted tightly into rather wide capillary tubing, attached rigidly to a block of wood. This arrangement allowed of the placing of the resistance in any desired position between the poles of the electromagnet.

The nickel wire—supplied by Hartmann and Braun, Frankfort—was about .5 cm. long and .0015 cm. diameter. Its resistance at 18° C. was 3.5173 ohms.

An electromagnet was used for supplying the magnetic field and, as the resistance was of very small dimensions, fairly large fields could be employed. The cross-section of the pole-pieces was large enough to ensure fairly uniform fields round the resistance. The resistance was measured by a Wheatstone bridge method—a compensating nickel resistance and two manganin resistances in oil formed the other three arms of the bridge. Deflexions of the galvanometer were noted instead of obtaining a balance every time and, as the galvanometer was calibrated before and after the experiments, this method proved quite satisfactory. There was a slight creep of the spot of light owing to

\* Communicated by Sir J. J. Thomson, O.M., F.R.S.

temperature change of the nickel, as the compensating nickel resistance was of slightly larger resistance than the one under observation. This creep was corrected for in the results obtained.

Experiments were carried out at the temperature of the room  $18^{\circ}\text{C}$ . and at a temperature of  $93^{\circ}\cdot 5^{\circ}\text{C}$ . This latter temperature was obtained by enclosing the nickel in a glass tube round which steam was passed. Liquid air was also used, but the low temperature affected the nickel wire in such a way, that the strain caused by switching on the magnetic field was sufficient to snap the wire. In all the experiments the wire was demagnetized by reversals before any readings were taken.

### *Longitudinal Field.*

Fig. 1, Pl. X. shows the curve obtained when the nickel was placed in the field longitudinally. The resistance increases fairly rapidly with the magnetic field until  $H = 350$ , then the increase becomes much less rapid until  $H = 1000$ , when a maximum increase in resistance is observed. After  $H = 1000$ ,  $\frac{dR}{R}$  decreases slightly, but this is probably due to the resistance being incorrectly placed in the longitudinal field. An error in setting of  $1^{\circ}\cdot 5$  would account for the decrease, and in one experiment it was absent altogether. It was thought possible that with a constant magnetic field the resistance might vary with the electric force, *i.e.* with the current. Currents varying from  $\cdot 1$  to  $\cdot 001$  ampere were used, but  $\frac{dR}{R}$  was found to be constant within these limits.

Fig. 2, Pl. X. shows a complete hysteresis cycle. The loops are to be expected on account of the slight decrease of resistance after reaching the maximum. The resistance alteration shows a distinct lag, and does not reach zero until a reverse field of  $H = 50$  is reached, after which  $\frac{dR}{R}$  becomes negative before commencing to increase again at  $H = 72$ .

Fig. 3, Pl. X. shows the hysteresis curve at a temperature of  $93^{\circ}\cdot 5^{\circ}\text{C}$ . The maximum resistance increase occurs at  $H = 320$ , a much lower value than is necessary at the ordinary temperature. The decrease, after reaching a maximum, is much greater than before and cannot be explained away so easily.

Fig. 4, Pl. X. shows the effect of a transverse magnetic field

on a nickel resistance. There is a slight preliminary increase, after which the resistance decreases uniformly until  $H = 1800$ , when the rate of decrease diminishes but does not reach a maximum. The form of the curve suggests that the increase is due to at least two distinct factors. One of these gives a decrease of resistance directly proportional to  $H$  until  $H = 1800$ , while the other gives an increase of resistance and soon reaches a maximum. On the assumption that such is the case the data for figure 5 have been calculated.

Fig. 5, Pl. X. shows the increase of resistance in a transverse magnetic field, which would result if the second factor, which gives a decrease of resistance, were absent. The shape of the curve is similar to that of figure 1 and the increase reaches a maximum in both curves at the same field strength. As the increase in resistance in figure 4 is approximately one-half of that of figure 1, it is probable that the cause of the increase of resistance in a longitudinal field is the same as is operative in the case of the preliminary resistance increase in a transverse field. This view is strengthened by consideration of figures 6 and 7.

Fig. 6, Pl. X. shows the transverse effect at  $93^{\circ}5$  C.

Fig. 7, Pl. X. shows the increase in resistance due to a transverse field at temperature  $93^{\circ}5$  C. Comparing figures 4 and 7 we notice that the maximum increase in a transverse field at  $93^{\circ}5$  C. is about one-half of what it is in a longitudinal field at  $93^{\circ}5$  C., and that the maximum increase occurs at the same field strength in both cases.

Figs. 8 and 9, Pl. X. show the hysteresis curves for the resistance effects in a transverse field at temperatures  $18^{\circ}$  C. and  $93^{\circ}5$  C. respectively. The difference in the curves is interesting.

It will be advantageous at this point to describe some experiments carried out by the author a short time ago on the elongation effect of a longitudinal magnetic field on a nickel rod. The method used—suggested by Dr. Swann—was that of placing a pure nickel rod inside a solenoid and observing the length alteration by means of interference fringes. The solenoid was so constructed as to allow of a flow of water between the wire and the rod, while the rod was firmly fastened at one end.

Fig. 10, Pl. X. shows the hysteresis curve so obtained. Unfortunately the magnitude of the field used was not large, but Bidwell\* has obtained results for large field values, and

\* Phil. Trans. 1888.



his results are in fair agreement for small field values with those now obtained. The loop in the curve is peculiar, but its presence seems certain as Dr. Swann has previously noticed it, and it was observed in every experiment which the author carried out.

Fig. 11, Pl. X. shows the elongation effect under a gradually increasing magnetic field. The large field values are taken from Bidwell's results. It will be observed that the maximum elongation effect occurs at a field strength of about 850, which is not far removed from the field strength which gives the maximum resistance increase effect.

Fig. 12, Pl. X. shows a remarkable relation between the two effects, which holds for all small field values. The points on the curve are obtained by noting the corresponding values of  $\frac{dR}{R}$  and  $-\frac{dl}{l}$  for gradually increasing field values, and then plotting  $\frac{dR}{R}$  against  $-\sqrt{\frac{dl}{l}}$ . The graph is a straight line at  $45^\circ$  to the axes for all small values of  $H$ . After  $H = 80$ ,  $\frac{dR}{R}$  increases more quickly than does  $\sqrt{\frac{dl}{l}}$ .

### *Discussion of Results.*

In his 'Corpuscular Theory of Matter' Thomson puts forward two theories of the method of conduction in solids. On the first of these the current is carried by free electrons while on the second it is carried by a transmission of electrons from atom to atom which are supposed to be orientated by the electric field. On the first theory the following is deduced :

$$\text{Resistance} = \frac{4 \alpha \theta}{\beta n e^2 \lambda v},$$

$$\text{or } R = \frac{K}{n \lambda v}, \text{ where } K \text{ is a constant.}$$

Thus any alteration of resistance on switching on the magnetic field must be due to an alteration of  $n$ ,  $\lambda$  or  $v$ . Of these three an alteration of  $\lambda$  seems the most probable. Adams\* has shown that in a transverse field,

$$\frac{dR}{R} = \frac{dT}{T} - \frac{1}{4} H^2 \frac{e^2}{m^2} T^2$$

\* Physical Review, 1907.

where  $T$  is the mean free period of the corpuscle and consequently  $= \frac{\lambda}{v}$ . In a longitudinal field the second term disappears and we get

$$\frac{dR}{R} = \frac{d\lambda}{\lambda} - \frac{dv}{v}.$$

As is shown in figure 11 the switching on of a magnetic field causes a dimensional change and it seems probable that this change is accompanied by a change of mean free path. From Nagaoka and Honda's experiments we know that the volume alteration is negligibly small compared with the length and cross-section changes. Calculating the cross-section changes on the assumption that the volume change is zero, it is possible to obtain a rough estimate of the mean free path changes in different directions, corresponding to certain dimensional changes. Such calculations show that a dimensional change give a variation of mean free path of the same order. The resistance change and dimensional change are not, however, of the same order. Even should  $R$  vary as  $\frac{1}{\lambda^2}$  or  $\frac{1}{\lambda^3}$  the resistance change would only be  $-2$  or  $-3$  times that of the mean free path change. It does not seem probable therefore that the alteration in length is the cause of the conductivity change. There is, however, probably some relation between the two, as figure 12 indicates. The following also point to some connexion.

As saturation point is approached both effects diminish rapidly.

There is little difference between the field strengths which give maximum effects in both cases.

An increase in temperature gives a diminished resistance effect for a given magnetic field while Bidwell observed a similar effect with respect to the elongation effect. Some such connexion as both being dependent on a third factor would explain the similarities of the two effects. This view is strengthened by the following considerations. In a longitudinal magnetic field nickel shows a continuous decrease in length and a continuous increase in resistance. Iron shows an increase in length at first, after which it commences to decrease until a saturation value is reached. Its resistance change, however, shows a decrease at first and afterwards an increase.

Such a thing as an alteration in configuration of the atom might both alter the mean free path of the corpuscles and diminish the number of corpuscles which carry the

current. The resistance would be altered if the velocity of the corpuscles carrying the current were to change. Such an alteration of velocity might result upon a re-arrangement of the atoms. From such a re-arrangement one might expect slight velocity changes but not changes of the order  $10^{-2}$ . As the velocity of the corpuscle is that due to its intrinsic energy and is not caused solely by its being pulled out of the atom by an adjacent atom; such changes of velocity could not be expected as the dimensional change is only of the order  $10^{-6}$  or  $10^{-5}$ .

From the equation

$$R = \frac{K}{n\lambda v},$$

we see that a decrease in  $n$ , i. e. the number of free corpuscles, would give an increase in  $R$ . The specific resistance is given by

$$R = \frac{4\alpha\theta}{\beta ne^2\lambda v}.$$

By calculation  $\lambda$  is found to be  $7 \times 10^{-9}$  approximately, and substituting the known values for the other quantities we find that  $n$  is of the order  $10^{32}$ . Thus to produce an alteration of the magnitude observed would require an absorption of  $10^{30}$  corpuscles, when a fairly strong magnetic field was applied. This means that each atom must absorb  $10^7$  corpuscles, which is unthinkable. The high value of  $n$  is of course improbable from considerations of specific heat. None of the factors therefore give a satisfactory explanation of the resistance change.

On the second theory of conduction the specific resistance is given by

$$R = \frac{9}{2} \frac{\alpha\theta}{e^2 dpNb}.$$

which reduces on substitution of known values to

$$R = \frac{1}{3.5 \times 10^{-12} pb}$$

where  $p$  is the number of corpuscles discharged per second per atom and  $b$  the distance between the centres of the doublets. The change in " $b$ " will be of the same order as the dimensional change and can be neglected in discussing the resistance alteration. Variation of " $p$ " is the most likely cause of the resistance change. Substituting for " $b$ "

its approximate value  $\frac{1}{\sqrt[3]{N}}$  we find that " $p$ " is of the order

$10^{23}$ . This is exceedingly large and indicates an internal radioactivity far greater than any external radioactivity of which we have experience. It is quite possible, however, that the ease with which corpuscles pass from one atom to another in close proximity to it, is incomparably greater than the ease with which a corpuscle leaves an atom and flies into space. If such a transference of corpuscles actually does take place it is conceivable that the re-arrangement of atoms, which undoubtedly results upon the creation of a magnetic field, may cause a great diminution in the number of corpuscles which are so transferred. Moreover, after a certain field value the internal re-arrangement ceases and one would therefore expect to find a maximum value for the resistance effect.

All metals show a slight resistance change in a magnetic field but those which are very susceptible to magnetic influence show far greater effects than others, *i. e.* those metals whose internal structures are easily altered show the greatest resistance change. Such a diminution in transference of corpuscles as has been suggested would result in increased resistance whether the nickel were placed in the field transversely or longitudinally. This actually is the case as the diminution observed in large transverse fields is due to another factor. If the change were due to an alteration of mean free path, then the two effects would be of opposite signs, as the length of the wire is diminished in longitudinal fields and increased in transverse ones. We may therefore conclude that a magnetic field causes a re-arrangement of the atoms which results in a dimensional change and a diminution of "internal" radioactivity. To this latter factor the resistance change is due. As the dimensional change and the resistance change are both due to the atomic re-arrangement we should naturally expect to find a similarity between the two effects; figure 12 shows that such similarity exists.

### *The Transverse Effect.*

The second part of the transverse effect has a different origin from the first and has no analogue in the longitudinal effect. Thomson\* deduced theoretically that an effect proportional to  $H^2$  was to be expected in a transverse field,

\* Internationale Congrès de Paris, 1900.



and Adams gives the following equation as expressing the result

$$\begin{aligned}\frac{dR}{R} &= -\frac{1}{4} H^2 \frac{e^2}{m^2} T^2, \\ &= -\frac{1}{4} H^2 \frac{e^2 \lambda^2}{m^2 v^2} \\ &= -\frac{1}{3} H^2 \times 10^{-16} \quad \text{approximately.}\end{aligned}$$

For a field of  $H=1000$  we get

$$\frac{dR}{R} = -\frac{1}{3} \times 10^{-10}.$$

The effect observed is of the order  $10^{-2}$ , and although the value of  $\lambda$  used is not certain, the difference between the observed and calculated values is far too great to be accounted for by an error in  $\lambda$ . To reconcile theory and experiment  $\lambda$  would have to be  $5 \times 10^{-5}$  cm., *i. e.* more than five times greater than the mean free path of a molecule in air. Such a result is extremely improbable and we must conclude that the effect observed is not that given by Adams' equation. Moreover the resistance increase is not proportional to the square of the field strength. The effect in iron is so much greater than in other metals as to call for some special explanation. Heaps\* has measured the effect in other metals and finds it to be represented by  $AH^2$  where  $A$  is of the order  $10^{-12}$ . This gives  $\lambda=10^{-6}$  approximately which is still very large. A longitudinal effect of the same order is observed in these other metals, and its existence leads one to surmise that the small effect observed in the non-magnetic elements is not the one which has been theoretically deduced. The first term of Adams' equation would give an effect in a longitudinal field, but the fact that the effects in both fields are of the same order of magnitude, and the large value of  $\lambda$  which has to be assumed to reconcile theory and experiment, points to a common origin for the two phenomena in the case of non-magnetic elements. On the other hand, in the case of nickel the two effects possess different characteristics. The longitudinal effect reaches a maximum with a comparatively small field value while the second part of the transverse effect does not reach a limiting value. Abnormally large values of the effect are observed in the cases of iron, nickel, and bismuth. The

\* Phil. Mag. 1912.

obvious explanation of this for the first two is their magnetic properties, but several reasons militate against this.

If the magnetic properties were the origin of the effect one would expect a far greater effect in the case of iron than in the case of nickel, but such is not the case. Moreover the magnetic properties reach saturation values at field strengths which give no saturation value to the resistance effect. Both the magnetic properties and the resistance effect may be due to the ease with which structural alterations take place in metals which give large effects, but the one is probably not the cause of the other. The dimensional change, the resistance effect and the magnetic properties may be due to a structural alteration such as is given in a longitudinal field. In addition to this it is possible that when the electric field is on and the doublets are orientated transversely to the magnetic field, then a further steady and continuous structural alteration takes place, which gives rise to an increase of internal radioactivity and a consequent diminution of resistance.

*Summary.*

- i. Hysteresis curves for both longitudinal and transverse fields at different temperatures have been obtained.
- ii. The effect in a transverse field is shown to consist of two parts, one of which gives an increase and reaches a maximum, and a second which gives a decrease and does not reach a maximum.
- iii. The longitudinal effect and the first part of the transverse effect possess similar characteristics.
- iv. There is some relation between the dimensional change in a magnetic field and the resistance effect but one is not the cause of the other.
- v. Both are probably resultant on a structural alteration.
- vi. The ordinary theory for the effect in a transverse field does not explain the results obtained. The effect is possibly due to a further structural change.

In conclusion I wish to express my thanks to Dr. Hicks for his interest in the work and for kind permission to use his laboratories.

My thanks are also due to Professor Sir J. J. Thomson and Dr. Swann for their interest in the work.

Cavendish Laboratory,  
Cambridge.

LXXXV. *The Theory of Molecular Volumes.*  
By GERVAISE LE BAS, B.Sc.\*

PART II.

CONSTITUTIVE EFFECTS IN MOLECULAR VOLUMES.

(a) *The Influence of Homology and the Symmetry of Radicles.*

THIS is a large subject and it permits of only a general treatment in this paper. It is remarkable that whilst laborious attempts have been made to show that molecular volumes are not a distinctively additive property, no one has hitherto attempted to discuss the nature of the constitutive influences operating on the volumes from the point of view of Kopp.

One of the first which calls for treatment is the effect of the addition of the homologous increment  $\text{CH}_2$ . We owe the first recognition of the gradual increase in the differences between two successive terms in a series to Schiff, Lossen & Zander, Gartenmeister, from a study of the aliphatic esters (*Annalen*, 233. p. 249, 1886), and Döbriner from a study of the ethers (*Annalen*, 243. p. 1, 1886).

Lossen has subsequently (*Annalen*, 254. p. 42, 1889) taken up the subject and devised a number of formulæ to better account for the volumes of the members of an homologous series.

Thus for the Formic Esters the formula is

$$V_m = 10.45 (\text{C})_m + 5.225 (\text{H})_n + 10.45 (\text{O})_o + 0.25 \frac{(n-2)^2}{2},$$

assuming that  $\text{C}=\text{O}=2\text{H}$ , and also that the increase is rectilinear from Methyl Formate onwards.

The following formula is based upon a better knowledge of the mode of variation of the atomic volumes, and the assumption is also made that  $\text{C}=4\text{H}$ ,  $\text{O}'=2\text{H}$ ,  $\text{O}''=3\text{H}$ .

$$V_m = (6n + 5) \{ 3.645 + (6n - 30) \times 0.0037 \}.$$

3.645 is the minimum volume of H, viz. at  $W \dagger = 35$  ( $\text{HCO}_2\text{C}_4\text{H}_9$ ). 0.0037 is the increment per H equivalent  $0.0037 \times 6 = 0.0222$  for  $\text{CH}_2$ . The formula does not apply to the first three compounds as may be seen from the curve.

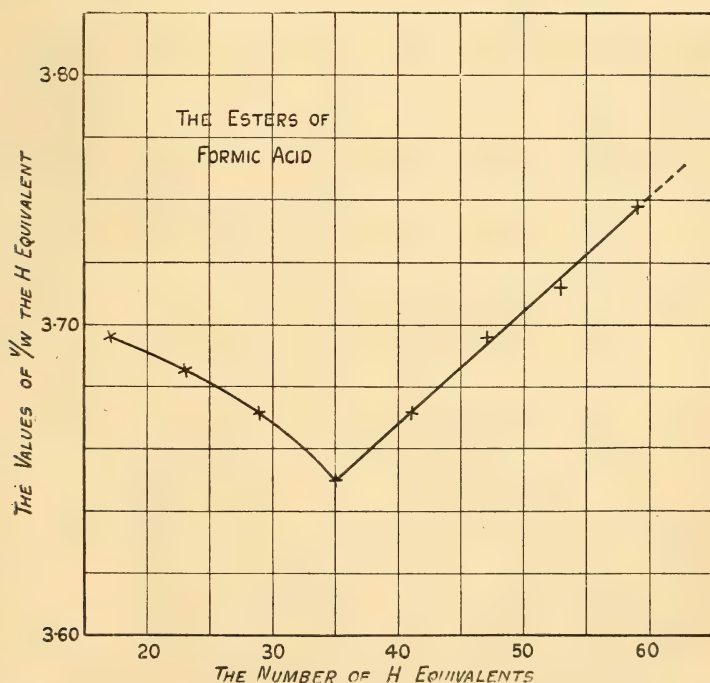
The variation of the atomic volumes is very different from what Lossen supposed, albeit rectilinear, starting from the 4th term.

\* Communicated by Prof. W. J. Pope, F.R.S.

† W represents the number of H equivalents.

## Volumes of the Formic Esters.

Compound.	W.	M. V. (obs.).	V/W.	M. V. (Le Bas).	M. V. (Lossen).
Methyl Formate, $\text{HCO}_2\text{CH}_3$ .....	17	62.7	3.688	...	62.7
Ethyl     " $\text{HCO}_2\text{C}_2\text{H}_5$ .....	23	84.6	3.678	...	83.85
Propyl    " $\text{HCO}_2\text{C}_3\text{H}_7$ .....	29	106.2	3.666	...	105.5
Butyl     " $\text{HCO}_2\text{C}_4\text{H}_9$ .....	35	127.6	3.645	127.57	127.65
Amyl     " $\text{HCO}_2\text{C}_5\text{H}_{11}$ ...	41	150.5	3.671	150.35	150.3
Hexyl     " $\text{HCO}_2\text{C}_6\text{H}_{13}$ ...	47	173.3	3.688	173.38	173.45
Heptyl    " $\text{HCO}_2\text{C}_7\text{H}_{15}$ ...	53	196.7	3.711	196.68	196.9
Octyl     " $\text{HCO}_2\text{C}_8\text{H}_{17}$ ...	59	220.3	3.734	220.25	221.25



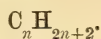
The value of  $V/W$ , which is the volume of H, first diminishes to  $\text{H} \cdot \text{COOC}_4\text{H}_9$   $W=35$ , and then increases in a straight line from that point quite abruptly.

Most of the curves possess features similar to the foregoing, but are somewhat different in form.

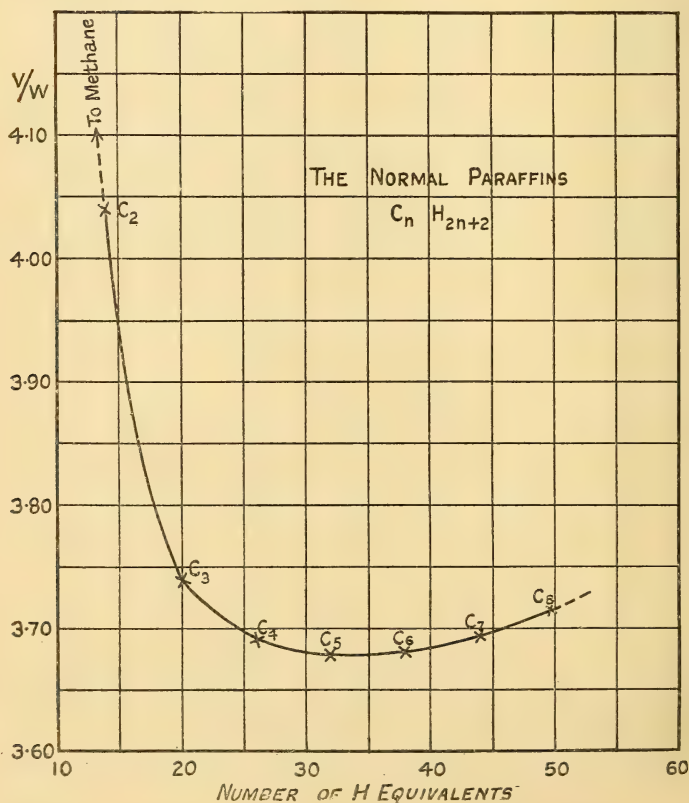
An interesting curve is that of the normal Paraffins, which unfortunately extends only to  $\text{C}_8\text{H}_{20}$ .



Mr. Gervaise Le Bas on the  
Molecular Volumes of the normal Paraffins.



Compound.	W.	M.V.	V/W.
Methane, $CH_4$ .....	8	38.4	4.800
Ethane, $C_2H_6$ .....	14	56.5	4.040
Propane, $C_3H_8$ .....	20	74.8	3.740
Butane, $C_4H_{10}$ .....	26	96.0	3.693
Pentane, $C_5H_{12}$ .....	32	117.8	3.681
Hexane, $C_6H_{14}$ .....	38	139.93	3.682
Heptane, $C_7H_{16}$ .....	44	162.56	3.695
Octane, $C_8H_{18}$ .....	50	186.26	3.725



This curve is a much wider one and very regular. The variation of  $V/W$  is at first very rapid, and then gradually

diminishes to a minimum at  $C_5$ . Afterwards the curve increases, but how, it is impossible to say exactly.

Similar to the above are the curves for the Halogen derivatives of the Paraffins &c.

*Related Series and the Effect of Symmetry.*

(a) The Aliphatic Esters.

Some preliminary work has been done on related series, *e. g.*, the esters of the Fatty Acids  $R-CO \cdot OR'$  studied by Gartenmeister and the Aliphatic Ethers by Döbriner, and some very significant relations have been obtained.

One of the curves, *viz.* that for the Esters of Formic Acid, has been shown.

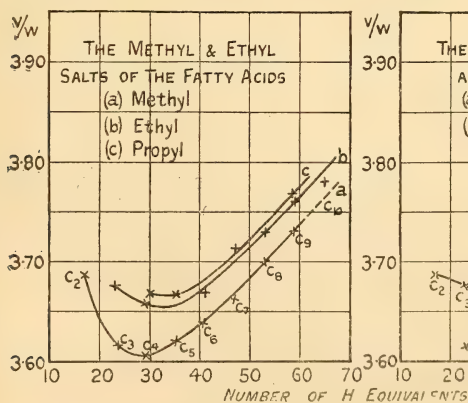
*The Methyl and Ethyl Salts of the Fatty Acids.*

METHYL.

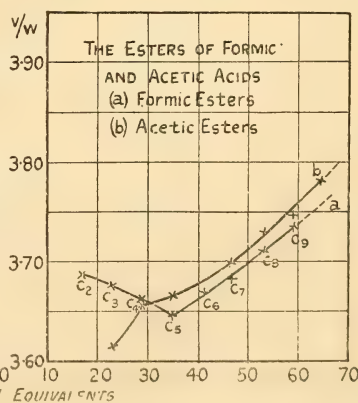
ETHYL.

Compound.	W.	M.V.	V/W.	Compound.	W.	M.V.	V/W.
H. COO CH <sub>3</sub> .....	17	62.7	3.688	H. COO C <sub>2</sub> H <sub>5</sub> .....	23	84.6	3.678
CH <sub>3</sub> . COO CH <sub>3</sub> .....	23	83.2	3.617	CH <sub>3</sub> . COO C <sub>2</sub> H <sub>5</sub> .....	29	106.1	3.659
C <sub>2</sub> H <sub>5</sub> . COO CH <sub>3</sub> .....	29	104.6	3.607	C <sub>2</sub> H <sub>5</sub> . COO C <sub>2</sub> H <sub>5</sub> .....	35	127.7	3.649
C <sub>3</sub> H <sub>7</sub> . COO CH <sub>3</sub> .....	35	126.7	3.620	C <sub>3</sub> H <sub>7</sub> . COO C <sub>2</sub> H <sub>5</sub> .....	41	150.5	3.670
C <sub>4</sub> H <sub>9</sub> . COO CH <sub>3</sub> .....	41	149.1	3.637	C <sub>4</sub> H <sub>9</sub> . COO C <sub>2</sub> H <sub>5</sub> .....	47	174.5	3.713
C <sub>5</sub> H <sub>11</sub> . COO CH <sub>3</sub> .....	47	172.2	3.662	C <sub>5</sub> H <sub>11</sub> . COO C <sub>2</sub> H <sub>5</sub> ...	53	197.7	3.730
C <sub>6</sub> H <sub>13</sub> . COO CH <sub>3</sub> .....	53	196.2	3.702	C <sub>6</sub> H <sub>13</sub> . COO C <sub>2</sub> H <sub>5</sub> ...	59	221.9	3.761
C <sub>7</sub> H <sub>15</sub> . COO CH <sub>3</sub> .....	59	220.1	3.732	C <sub>7</sub> H <sub>15</sub> . COO C <sub>2</sub> H <sub>5</sub> ...	65	245.9	3.782

A.



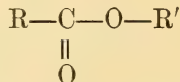
B.



It will be useful to reproduce some of the curves in order to show how these various series develop. We consider first the methyl and ethyl salts of the fatty acids. It can

easily be shown that considerable irregularities occur in the data, so that we are under the necessity of smoothing the curves.

The accompanying diagrams show how the values of  $V/W$  vary in



(a) according as R is increased in complexity,

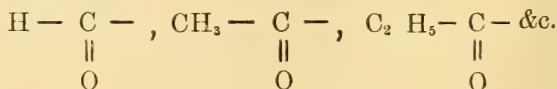
(b) according as R' is increased in complexity.

Diagram A gives the methyl, ethyl, and propyl salts of the different fatty acids.

Diagram B gives the different salts of the various acids, formic and acetic.

There is a striking difference between them.

Diagram A shows regular open curves which are similar to that for the paraffins. This is the effect one would expect, seeing that the radicle of increasing complexity R is attached to a carbon atom (the C radicle). The similarity of the two series is increased by the fact that in the methyl curve we have successively



combinations similar to  $\text{H}-\text{CH}_3$ ,  $\text{CH}_3-\text{CH}_3$ ,  $\text{C}_2\text{H}_5-\text{CH}_3$ . In consequence of this we find that the initial part of the methyl curve shows a rapid decrease before the minimum. The actual values are of course depressed owing to the influence of  $-\text{OCH}_3$ .

All the methyl salts are smaller in volume than the corresponding (metameric) ethyl salts, and the latter slightly smaller than the propyl. This question will be considered later.

Turning to Diagram B we find quite a different result. The increase in complexity is connected with the O radicle—that is, the curves show the variation of  $V/W$  when  $-\text{O}-\text{R}$  increases in complexity. The C radicle remains constant.

We note first the unique character of the curve for the esters of formic acid.

If we compare this in its earlier stages with the acetic ester curve we note how the influence of  $\text{H}-\text{C}$  is exerted in



raising the value of  $V/W$  just as the value for  $\text{H}-\text{CH}_3$  is exceptionally high. This is in spite of the presence of the

simple O radicles  $-\text{OCH}_3$ ,  $-\text{OC}_2\text{H}_5$ ,  $-\text{OC}_3\text{H}_7$ ; that is, the elevating influence of this more than counterbalances the depressing influences of the latter.

The Acetic Esters on the other hand show the depressing influence of  $-\text{OCH}_3$ , as do the esters of the other fatty acids which include  $-\text{O} \cdot \text{CH}_3$ . The remaining part of the curve resembles corresponding curves for the Ethers, which are also distinguished by the presence of an O radicle.

Thus the development of the

C radicle is similar in result to the Paraffin curves,

and the development of the

O radicle resembles in effect the Ether curves (vide prox.).

This indicates the importance of the effect of the typical atoms C and O.

### The Influence of Symmetry.

It has been shown that the methyl, ethyl, and probably the propyl salts of the fatty acids have more or less depressed values of  $V/W$ ; and this at once introduces the effect of symmetry on molecular volumes. By symmetry we mean the disposition of the C atoms on one side and the other of the typical atom or group—in this case  $-\text{C}-\text{O}-$ .



Owing to some irregularities in the data, it will be of advantage to read off the values of  $V/W$  from the curves. The following numbers indicate the typical effect in the variation in volume with variation in symmetry.

### Isomeric Esters.

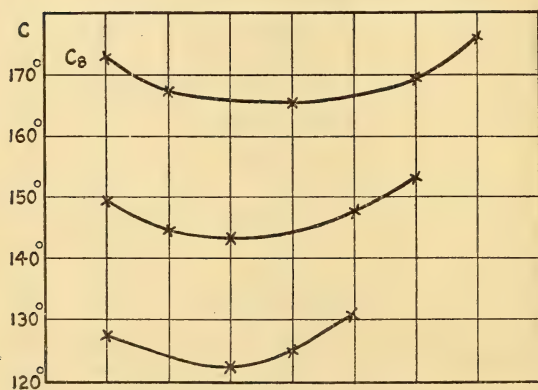
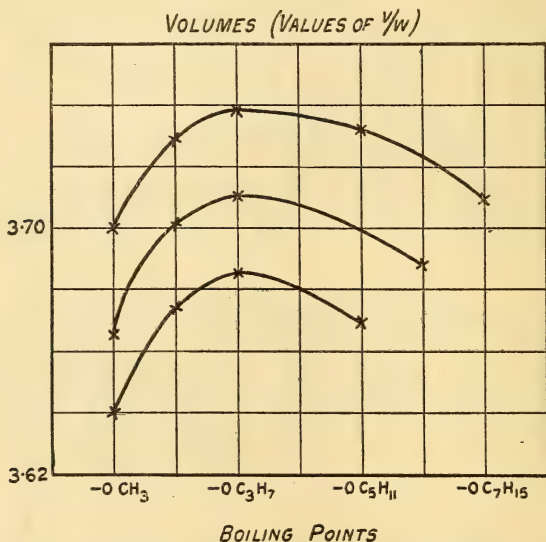


	M.V.	B.P.
Methyl Heptylate, $\text{C}_6\text{H}_{13} \cdot \text{CO} \cdot \text{OCH}_3$ .....	196.2	173
Ethyl Caproate, $\text{C}_5\text{H}_{11} \cdot \text{CO} \cdot \text{OC}_2\text{H}_5$ .....	197.7	167
Propyl Valerate, $\text{C}_4\text{H}_9 \cdot \text{CO} \cdot \text{OC}_3\text{H}_7$ .....	197.8	167
Butyl Butyrate, $\text{C}_3\text{H}_7 \cdot \text{CO} \cdot \text{OC}_4\text{H}_9$ .....	197.8	165.7
Hexyl Acetate, $\text{CH}_3 \cdot \text{CO} \cdot \text{OC}_6\text{H}_{13}$ .....	197.7	169
Heptyl Formate, $\text{H} \cdot \text{CO} \cdot \text{OC}_7\text{H}_{15}$ .....	196.7	176

It is seen that the most symmetrical compounds possess the largest volumes and the smallest B.P.'s. The volumes fall off towards either end, but more so in the direction of the simplest O radicle than in the direction of the simplest C radicle. The boiling-points correspondingly increase.



The following is a diagrammatic representation of the above constitutive effects, the upper curves being for the isomers  $C_8H_{16}O_2$ , and the succeeding ones those for the isomers  $C_7H_{14}O_2$  and  $C_6H_{12}O_2$  respectively.



The two families of curves are evidently related. That constitutive peculiarity which occasions an augmentation in the volumes depresses the boiling-point and *viceversa*.

These effects are usually attributed to *Symmetry*—that is, to similarity or dissimilarity in the O and C radicles. In any case the simple radicles  $CH_3$ ,  $C_2H_5$ , &c. in association with more complex radicles produce remarkable diminutions in volume according to the preceding diagrams, and corresponding elevations of the boiling-point.

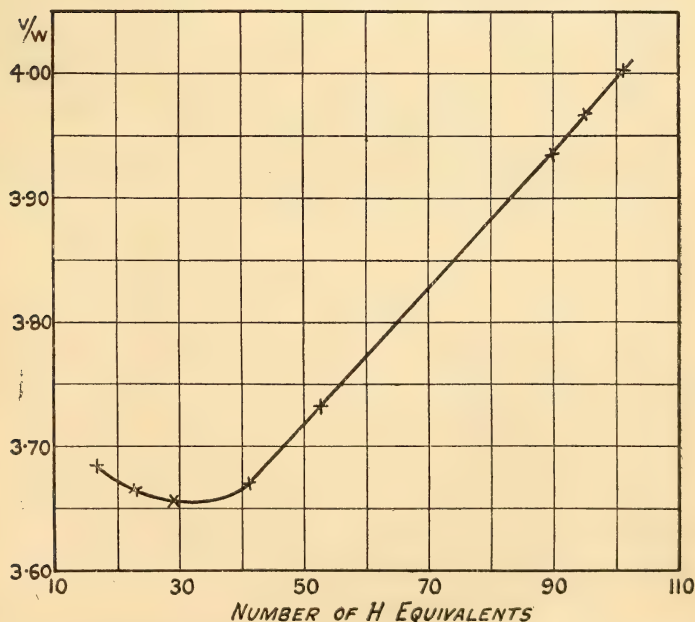
The curves are very similar to each other, showing that whatever may be the total length of the chains the effect of symmetry is the same.

The following is a list of the symmetrical esters :—

*Volumes of the Symmetrical Esters.*

Compound.	W.	M.V.	V/W.	$\Delta$ .
$C_7H_{15}-CO.O-C_8H_{17}$ .....	101	404.3	4.001	0.033
$C_7H_{15}-CO.O-C_7H_{15}$ .....	95	377.0	3.968	0.033
$C_6H_{13}-CO.O-C_7H_{15}$ .....	89	350.2	3.935	$6 \times 0.033$
.....	.....	.....	.....	
$C_3H_7-CO.O-C_4H_9$ .....	53	197.8	3.732	$2 \times 0.030$
$C_2H_5-CO.O-C_3H_7$ .....	47	150.6	3.673	
$C_2H_5-CO.O-C_2H_5$ .....	29	106.1	3.659	
H. $COOCH_3$ .....	17	62.7	3.688	

*The Values of V/W among the Symmetrical Esters.*



The most important feature of this curve is the rectilinear character of the portion succeeding the minimum.

*Related Series.*

## (b) The Aliphatic Ethers.

A second group of these series is found in the Ethers

$R-O-R'$ , which only contain O radicles.

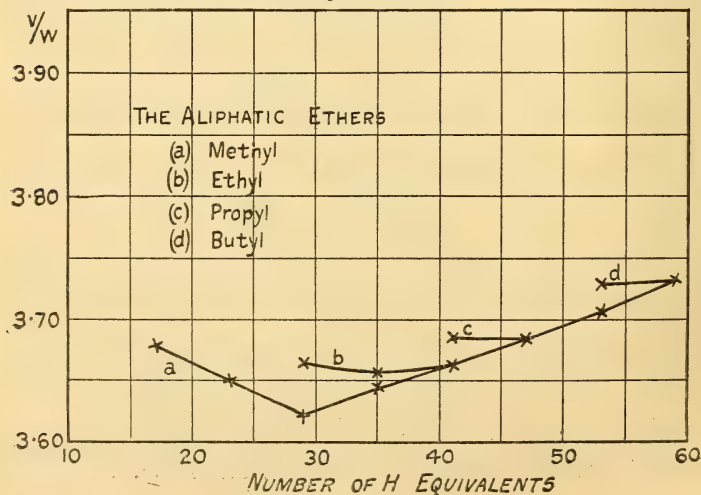
The most advantageous way of studying them is to begin with the symmetrical compound and then proceed to increase the complexity of one side. We thus keep the complexity of one side constant, and thus have the Methyl, Ethyl, Propyl, &c. Ethers.

*The Methyl Ethers.**The Ethyl Ethers.*

Compound.	W.	M.V.	V/W.	Compound.	W.	M.V.	V/W.
$CH_3.O.CH_3$ .....	17	62.56	3.680	$C_2H_5.O.C_2H_5$ .....	29	106.2	3.664
$CH_3.O.C_2H_5$ .....	23	84.0	3.652	$C_2H_5.O.C_3H_7$ .....	35	128.08	3.659
$CH_3.O.C_3H_7$ .....	29	105.1	3.624	$C_2H_5.O.C_4H_9$ .....	41	150.33	3.666
$CH_3.O.C_4H_9$ .....	35	127.5	3.643	$C_2H_5.O.C_5H_{11}$ ...	47	173.22	3.686
$CH_3.O.C_5H_{11}$ .....	41	150.2	3.664	$C_2H_5.O.C_6H_{13}$ ...	53	196.25	3.703
$CH_3.O.C_6H_{13}$ .....	47	173.15	3.685	$C_2H_5.O.C_7H_{15}$ ...	59	221.32	3.751
$CH_3.O.C_7H_{15}$ .....	53	196.47	3.706	$C_2H_5.O.C_8H_{17}$ ...	65	247.2	3.803
$CH.O.C_8H_{17}$ .....	59	220.2	3.733				

The other series can be tabulated in the same way. Döbriner, to whom we are indebted for the data, omitted all those with radicles  $C_5H_{11}$ — and  $C_6H_{13}$ —, but the essential ones can be supplied by interpolation.

The data give the following curves, which are in striking contrast with those shown by the esters :—

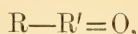


The curves form a system, which is strikingly regular. They should be similar to the curves derived from a gradual increase in the complexity of the O radicles in the salts of formic, acetic, &c., acids.

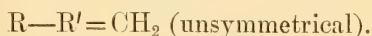
The methyl curve is exceedingly like the curve for the salts of formic acid, but the others are different.

### *The Effect of Symmetry.*

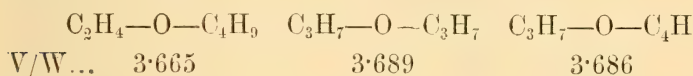
It is noted that there is a remarkable distinction to be drawn between the first member in each series (the symmetrical compound) for which



and the ones distinguished by the relation



Thus in the triplet

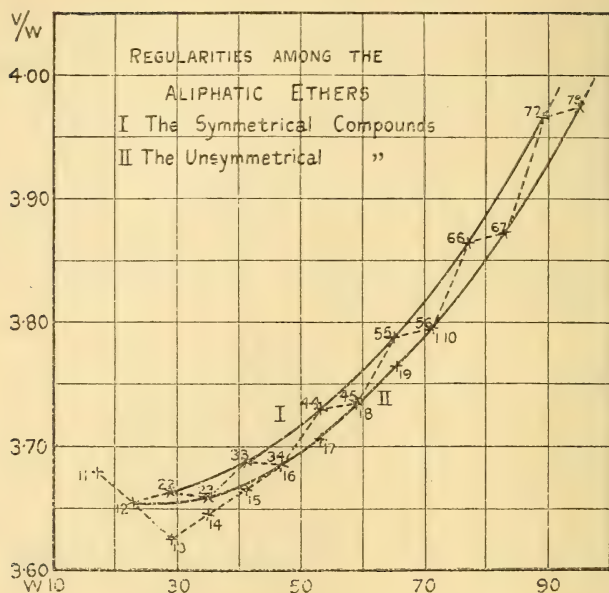


the first and second are different, although isomeric; the second and third similar in value, although of different complexity.

### *Volumes of the Ethers.*

Symmetrical.				Unsymmetrical.			
W.	Compound.	M.V.	V/W.	W.	Compound.	M.V.	V/W.
17	$CH_3.O.CH_3$ .....	62.56	3.680	23	$CH_3.O.C_2H_5$ .....	84.0	3.652
29	$C_2H_5.O.C_2H_5$ .....	106.2	3.664	35	$C_2H_5.O.C_3H_7$ ...	128.08	3.659
41	$C_3H_7.O.C_3H_7$ .....	151.27	3.689	47	$C_3H_7.O.C_4H_9$ ...	173.25	3.686
53	$C_4H_9.O.C_4H_9$ .....	197.72	3.730	59	$C_4H_9.O.C_5H_{11}$ ...	[220.35]	3.733
65	$C_5H_{11}.O.C_5H_{11}$ ...	[246.28]	3.789	71	$C_5H_{11}.O.C_6H_{13}$ ...	[269.44]	3.795
77	$C_6H_{13}.O.C_6H_{13}$ ...	[297.76]	3.867	83	$C_6H_{13}.O.C_7H_{15}$ ...	[321.21]	3.870
89	$C_7H_{15}.O.C_7H_{15}$ ...	353.42	3.970	95	$C_7H_{15}.O.C_8H_{17}$ ...	[377.60]	3.975





It is found that there are at least two influences at work :—

(a) The Effect of the Lengthening of the Hydrocarbon Chain.

By studying the curve for the *symmetrical* compounds we find that the constitutive effect depends upon the *cube of the length of chain* and the volume of the atoms as measured by  $V/W$  upon the square.

Thus the total correction is

$$\Delta_1 = (6n + 5) \left( \frac{n-4}{2} \cdot \frac{n-2}{2} \right) \times 0.0101 ;$$

$n$  represents the number of carbon atoms in the compound ;

$n-4$  the increase in the number above 4 which are found in  $C_2H_5 \cdot O \cdot C_2H_5$ , the compound first marked on the curve ;

0.0101 is a constant.

The *unsymmetrical compounds* follow a similar curve, and by finding the points on the upper curve corresponding to

these, we obtain the value of the correction for want of symmetry by difference.

This apparently depends on the *square* of the number of atoms at least for compounds of the type  $R-R'=CH_2$ .

The correction is

$$\Delta_2 = -(6n + 5) \times n_{\text{odd}} \times 0.003,$$

and the whole formula is

$$V_m = (6n + 5) \left[ 3.664 + 0.0101 \left( \frac{n}{2} - 2 \right) \left( \frac{n}{2} - 1 \right) - 0.003 n_{\text{odd}} \right].$$

By means of this formula, compounds of the type  $R-R'=O$  (symmetrical) and those of the type  $R-R'=CH_2$  (unsymmetrical) may have their volumes at the normal B.P. calculated.

*Calculation of the Volumes of the Symmetrical and Unsymmetrical Compounds.*

Class.	Compounds.	W.	n.	V/W.	Corr. for want of Symmetry.	V/W calc.	V/W obs.	V calc.	V obs.
S	$CH_3 \cdot O \cdot CH_3 \dots$	17	2	3.664		—	3.677	62.25	62.56
U	$CH_3 \cdot O \cdot C_2H_5 \dots$	23	3	3.661	-0.009	3.652	3.652	84.0	84.0
S	$C_2H_5 \cdot O \cdot C_2H_5 \dots$	29	4	3.664		3.664	3.664	106.25	106.2
U	$C_2H_5 \cdot O \cdot C_3H_7 \dots$	35	5	3.672	-0.015	3.657	3.659	128.00	128.08
S	$C_3H_7 \cdot O \cdot C_3H_7 \dots$	41	6	3.684		3.684	3.689	151.04	151.27
U	$C_3H_7 \cdot O \cdot C_4H_9 \dots$	47	7	3.705	-0.021	3.684	3.686	173.15	173.25
S	$C_4H_9 \cdot O \cdot C_4H_9 \dots$	53	8	3.725		3.725	3.730	197.42	197.72
U	$C_5H_{11} \cdot O \cdot C_5H_{11} \dots$	59	9	3.752	-0.027	3.725	3.733	219.77	220.35
S	$C_5H_{11} \cdot O \cdot C_6H_{13} \dots$	65	10	3.785		3.785	3.789	246.02	246.28
U	$C_6H_{13} \cdot O \cdot C_6H_{13} \dots$	71	11	3.823	-0.033	3.790	3.795	269.09	269.44
S	$C_6H_{13} \cdot O \cdot C_7H_{15} \dots$	77	12	3.866		3.866	3.867	297.68	297.76
U	$C_7H_{15} \cdot O \cdot C_7H_{15} \dots$	83	13	3.914	-0.039	3.875	3.870	321.62	321.21
S	$C_7H_{15} \cdot O \cdot C_8H_{17} \dots$	89	14	3.967		3.967	3.970	353.06	353.42
U	$C_8H_{17} \cdot O \cdot C_8H_{17} \dots$	95	15	4.025	-0.045	3.980	3.975	378.1	377.6

We have supposed, as is usual, that these variations are due to symmetry or want of it, but this explanation does not seem to be complete or even quite satisfactory. A more precise knowledge of the inner meaning of this constitutive variation may be eventually arrived at. This also applies to the meaning of the effect of variation with complexity.

LXXXVI. *Notices respecting New Books.*

*Collected Papers in Physics and Engineering.* By JAMES THOMSON, D.Sc., LL.D., F.R.S. Pp. civ + 484. Cambridge University Press, 1912.

THESE papers have been collected and arranged with unpublished material and brief annotations by Sir Joseph Larmor and James Thomson (the son). They are preceded by an introductory and biographical essay containing many details of great interest and by a reprint of an obituary notice written by Dr. J. T. Bottomley; also by a list of 28 scientific terms introduced by James Thomson. Though many of these have not been adopted (*e.g.* Crinal, funal, lesion, disply, expansity) yet amongst the rest there are many which are in everyday use, *e.g.* radian, interface, poundal, numeric, forcive, torque. Though he was overshadowed by his greater brother, yet he received due recognition of his work, which was that of a pioneer. He is no doubt best known for his theoretical work on congelation and liquefaction and by his contributions to the development of ideas in connexion with Dr Andrews' experiments on the continuity of the gas and liquid states. But the papers dealing with these important questions represent only a small fraction of his work; yet, because this work is mainly of an engineering type, it has inevitably been in part superseded by the tremendous developments which have since taken place in engineering theory and practice. No one opening these pages will fail to be struck by the great originality displayed in them. No one recognized this more than his brother Lord Kelvin, and it is very pleasing to see from the biographical notice how much the two brothers contributed to each other's work.

Many of the papers appeared in somewhat inaccessible journals and will be new to the majority of physicists. This fact makes their publication in collected form of more than usual interest.

*Department of Commerce. U. S. Coast and Geodetic Survey.*  
O. H. TITTMANN, Superintendent.

- (A) GEODESY. The California-Washington Arc of Primary Triangulation. By A. L. BALDWIN. Special Publication No13 (quarto pp. 78). Washington, 1913.

(A) This volume deals with the measurement of an arc extending over about 577 miles from  $39^{\circ} 5' N.$  to  $47^{\circ} 23' N.$ , near the meridian of  $122^{\circ} 30' W.$  The field observations were taken between 1903 and 1906. The volume is mainly occupied with observational details and descriptions of the stations. There are, however, some results of general interest relating to the degree of accuracy obtained. It is concluded that if the ascertained facts of atmospheric refraction are borne in mind, vertical angles can be measured with greater accuracy than is generally believed. Determinations, for instance, were made of the height of Mount Shasta involving the measurement of vertical angles from six

different bases. Four of the results lay between 4315.5 and 4316.6 metres, the other two being respectively 4309.0 and 4318.7. It is suggested that theodolite observations taken—usually in the afternoon—along a meridian may suffer from irregularity of heating as between the east and west sides of the instrument, and that this may account for a “twist” believed to exist in the present case.

- (B) ASTRONOMY. Determination of Time, Longitude, Latitude and Azimuth, 5th Edition. By WILLIAM BOWIE. Special Publication No. 14 (quarto pp. 177). Washington, 1913.

This is a revised and enlarged edition of a manual issued by the U.S. Coast and Geodetic Survey to “serve as a guide to the observer in the field and the computer in the office in carrying on the astronomic work of the Survey.” Except that it supposes the reader to refer to textbooks like Chauvenet’s for the proofs of the formulæ, it is practically a complete treatise on the astronomical side of survey work. There are 29 illustrations, showing various patterns of theodolites and their mountings, chronographs, signals and signal lamps, observing tents and marks of various kinds. The methods of observation and reduction are explained in detail with illustrations, and there are a number of useful tables.

## LXXXVII. *Intelligence and Miscellaneous Articles.*

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.  
COMMITTEE FOR RADIOTELEGRAPHIC INVESTIGATION.

### SPECIAL INVESTIGATION.

*Effect on the Propagation of Electric Waves of the Total Eclipse  
of the Sun, 21st August, 1914.*

THE forthcoming total eclipse of the sun affords an exceptional and important opportunity of adding to existing knowledge of the propagation of electric waves through air in sunlight and in darkness, and across the boundaries of illuminated and unilluminated regions. The eclipse will be total along a strip extending from Greenland across Norway, Sweden, Russia and Persia to the mouths of the Indus. In Russia the duration of totality will be a little more than two minutes.

There are two main points calling for investigation during the eclipse. In the first place, the propagation of signal-bearing waves through air in the umbra and penumbra will probably obey laws different as regards absorption and refraction from those obeyed in illuminated air. In the second place, the strength, frequency and character of natural electric waves, and of atmospheric discharges, may vary. The variations may occur either because the propagation of natural waves from distant sources is facilitated or impeded by the eclipse, or, possibly, because the production of natural electric waves or atmospheric discharges is for some unknown reason affected by the eclipse.



These points have previously been investigated to only a slight extent. The observers of signals during the solar eclipse of 17th April, 1912, nearly all agreed that the strength of the signals was greater during the eclipse than an hour before or after. There was only one special observation of strays during the same eclipse, when very pronounced and remarkable variations were recorded during the passage of the shadow-cone across Europe.

To investigate the propagation of signals across the umbra it will be necessary to arrange for wireless telegraph stations on either side of the central line of the eclipse to transmit signals at intervals while the umbra passes between them. This transit of the umbra occupies about two minutes. It is thus very desirable that the Scandinavian and Russian stations should transmit frequently throughout several minutes before, during, and after totality. But stations other than those favoured by their proximity to the central line should endeavour to keep a complete record of the variations of signals during the eclipse. Stations in Europe west of the central line and stations in the Mediterranean and in Asia Minor may find noticeable changes in the strength of signals, particularly long distance signals, between the hours of 10 a. m. and 3 p. m., Greenwich time; and it is probable that the stations of India and East Africa, and ships in the Indian Ocean, may feel the effect of the penumbra in the afternoon. On the other hand, ships in the Atlantic, and fixed stations in Eastern Canada and the United States, will probably be affected by the penumbra in the early morning. At Montreal the eclipse (partial) is at its greatest phase at 5.52 a. m. Standard Time. It is possible that the eclipse may have some influence even when it is invisible.

The investigation of strays is of as great interest as that of signals. So far as is yet known, the natural electric waves reaching wireless telegraph stations in latitudes higher than  $50^{\circ}$  appear to travel mostly from the south. Thus the greatest changes produced in strays by the eclipse will probably be experienced at stations in Scandinavia and Russia, to reach which the waves must cross the path of the umbra. At the same time changes of some kind are to be expected in other districts than these and it is therefore desirable that statistical observations of natural electric waves be made all over the world, and especially at places within an earth quadrant of Southern Russia. It is also desirable that meteorological observations, including those of atmospheric ionization and potential gradient, should be at the disposal of the Committee when considering the records of strays and signals.

The Committee propose to prepare and circulate special Forms for the collection of statistics of signals and strays, especially within the hemisphere likely to be affected by the eclipse; they will endeavour to make provision for the transmission of special signals at times to be indicated on the Forms; and they will offer for the consideration of the authorities controlling stations near the central line a simple programme of work. The discussion of the observations, and the comparison with meteorological data, will be carried out by the Committee; and digests of the statistics, together with the

conclusions drawn from the analysis, will be published in due course.

The Committee would be greatly aided in the organization of this investigation if those possessing the necessary facilities and willing to make observations during the eclipse would communicate with the Hon. Secretary, Dr. W. ECCLES, University College, London, W.C., at the earliest possible date.

ON THE RECOMBINATION OF IONS MADE BY  $\alpha$  RAYS.

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,

In a paper in the December number of the Philosophical Magazine Mr. Ogden describes some experiments on initial recombination of ions. As the exact nature of the effect appears to have not yet been made quite clear by the various experiments on the subject (Moulin's explanation is not sufficient), I would like to point out one of the causes operating (of which there are probably several) which would make a dense pencil of ions in a gas behave different from a uniform distribution. This may be helpful in carrying out further investigations on the subject. If each of the electrons ejected by the  $\alpha$  particle on the average does not form a cluster as the result of a single collision with a neutral molecule, there would exist initially principally general recombination between free negative ions or electrons and positive ions. The disappearance of ions would thus to a certain extent depend on the average period of life of an electron before forming a cluster, and on the coefficient of recombination of free electrons and positive ions. I have obtained experimental evidence that an electron undergoes a large number of collisions before it successfully forms a cluster, which will be dealt with fully in a paper which will appear shortly. The period of life of an electron and the coefficient of recombination of electrons and positive ions probably depend considerably on the nature of the gas. We do not know anything yet about the latter quantity, but it is probably greater than the coefficient of recombination measured in the usual way, in which case recombination occurs between negative clusters and electrons and the positive ions. This would explain the intense effects obtained.

Yours faithfully,  
R. D. KLEEMAN.

*To the Editors of the Philosophical Magazine.*

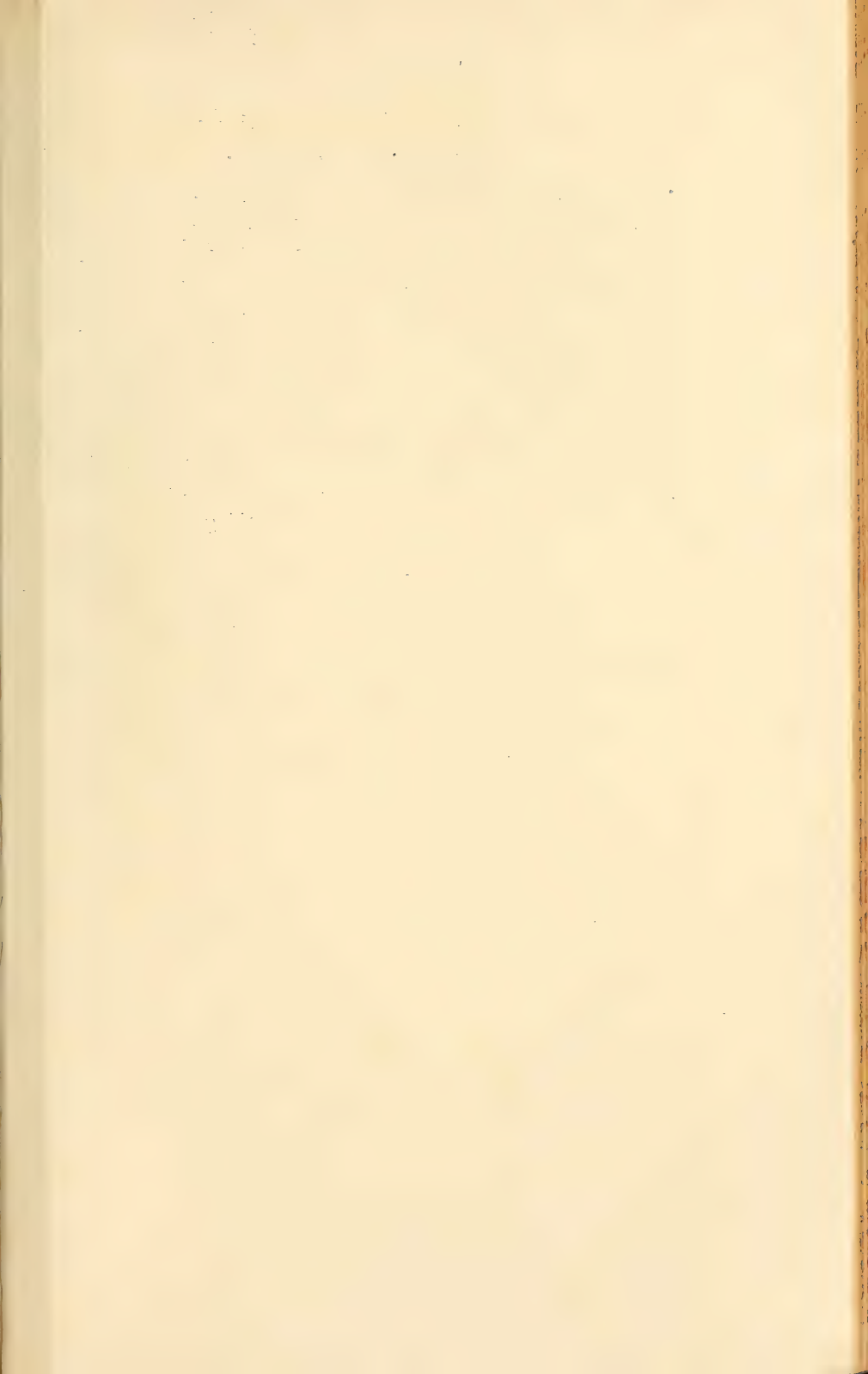
GENTLEMEN,

In a paper published in the Proceedings of the Royal Society, A. vol. 83, p. 376 (1909), I showed that the collision current between an aluminium plate and leaf in a gas at a pressure of

several mm. of mercury depends on the direction of the electric field applied, the initial ions being produced by a beam of  $\alpha$  particles shot through the aluminium leaf and ending its course in the aluminium plate. In a letter to the *Philosophical Magazine* of July, 1912, I pointed out that this effect would be produced if the electrons liberated from the gas molecules are projected more or less in the direction of propagation of the  $\alpha$  particles, and an ion undergoes a cycle of clustering in the gas during which for a time it is an elementary ion. Dr. Campbell, in a footnote to a paper published in the January number of the *Phil. Mag.*, says that since he finds no asymmetry in the number of electrons given off from the opposite surfaces of the metal plate and leaf, the electrons are not projected in the direction of motion of the ionizing  $\alpha$  particle. To obtain an insight into the reliability of such experiments, let us consider the experiments that have been carried out with ultra-violet light. The velocity of the ejected electrons is practically the same in the two cases. It was found that the quantity and quality of the electrons given off from a metal plate under the influence of ultra-violet light depended greatly on the smoothness of the surface of the plate, and even when polished depended greatly on the nature of the process of polishing employed; further, the sensitiveness of the surface changed with time. The experiments of various observers showed extraordinary discrepancies. It was in time found that only tolerably consistent results were obtained when at a low pressure the surface of a plate was removed by making it the anode in a discharge-tube, or depositing a new surface, or removing the surface by evaporation in the case of a liquid (such as mercury), and then taking the measurements without allowing the surface to come into contact with a gas at a high pressure. These processes remove the film of gas and oxide from the surface, and the matter deposited through polishing in the case of a plate. I therefore fail to see how much reliance can be placed on experiments of the nature carried out by Dr. Campbell unless the same precautions are taken. The difference between the number of electrons emitted from the two surfaces in the experiment is bound to be a small fraction of the total number emitted, and could therefore be easily rendered uncertain in sign by errors of the magnitude observed with ultra-violet light. It is not surprising therefore that Dr. Campbell did not obtain very consistent results. Moreover, in the interpretation of such experiments we must also not ignore the possibility that the process of ionization of a molecule in the solid state by an  $\alpha$  particle may be somewhat different from that when the molecule is in the gaseous state. The fact that a molecule is more easily ionized by ultra-violet light in the solid than in the gaseous state renders such a thing highly probable.

Yours faithfully,

R. D. KLEEMAN.





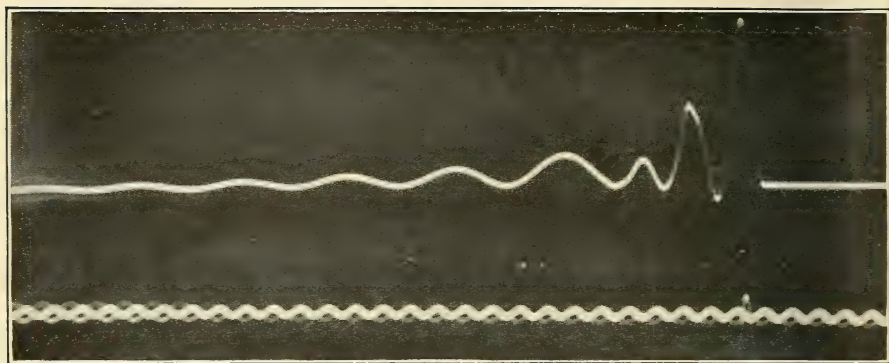


FIG. 4.—Condenser A, primary open. Sparking method.

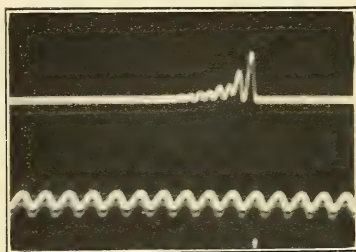


FIG. 5.—Condenser E, primary closed.  
Sparkling method.

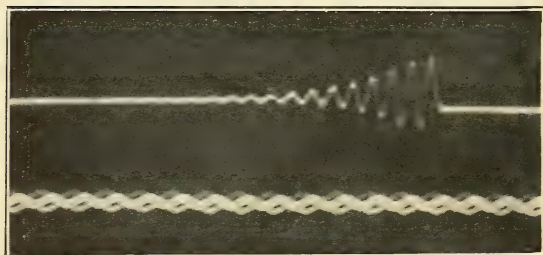


FIG. 6.—Short circuiting method. No condenser.

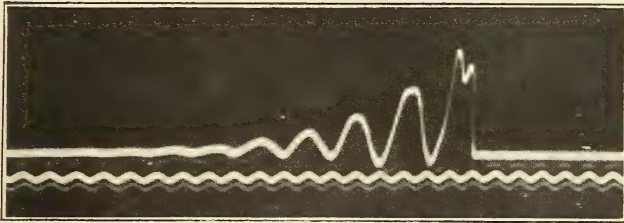


FIG. 7.—Case I.  $i_0 = 4$  amperes.

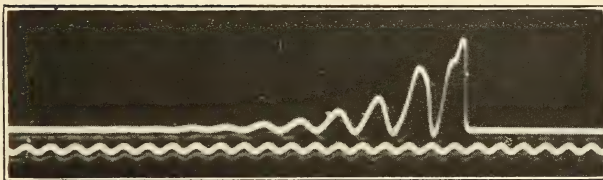


FIG. 8.—Case II.  $i_0 = 3$  amperes.

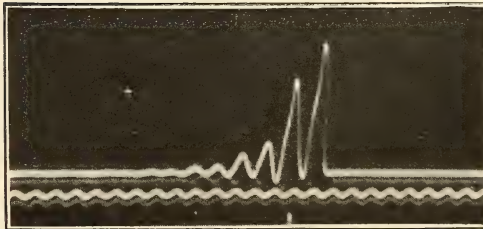
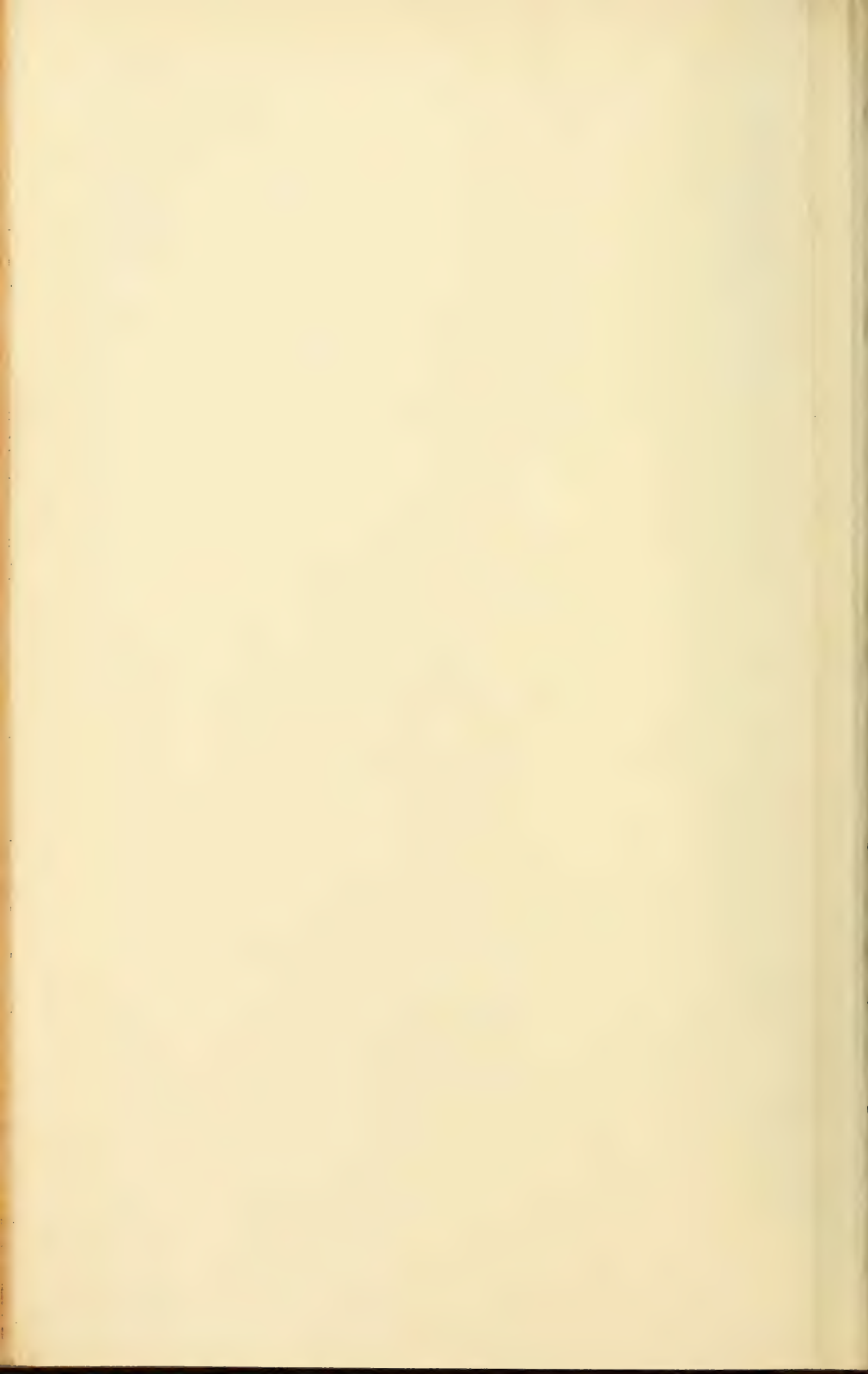


FIG. 9.—Case III.  $i_0 = 2.5$  amperes.



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Phil. Mag. Ser. 6, Vol. 27, Pl. IX.

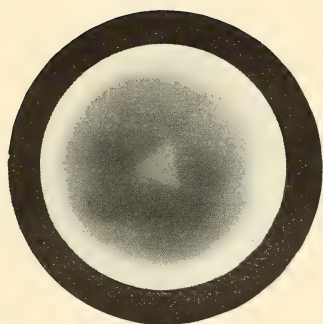






FIG. 11.

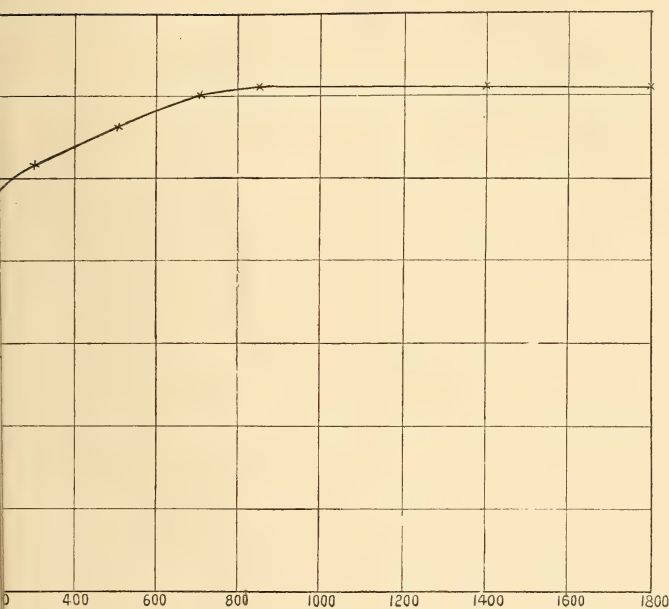


FIG. 12.

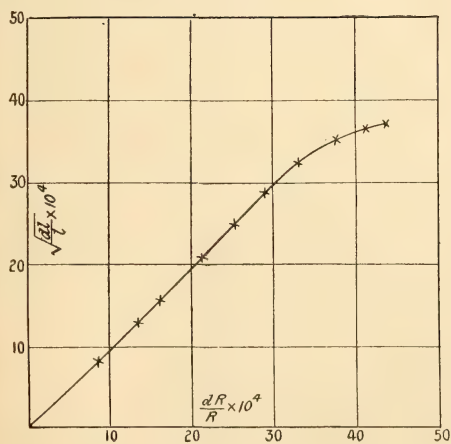




FIG. 1.

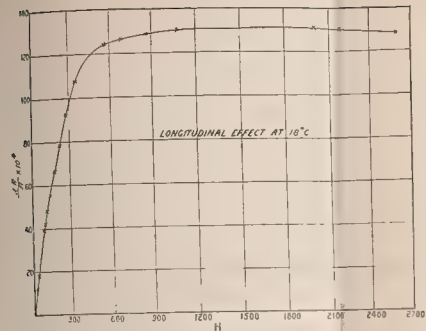


FIG. 3.

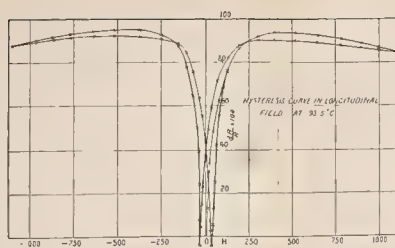


FIG. 5.

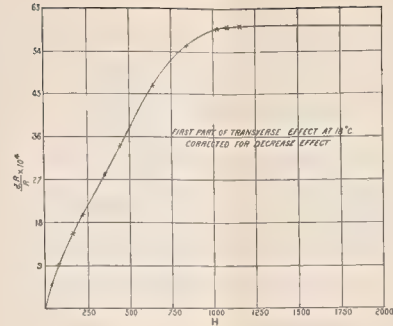


FIG. 7.

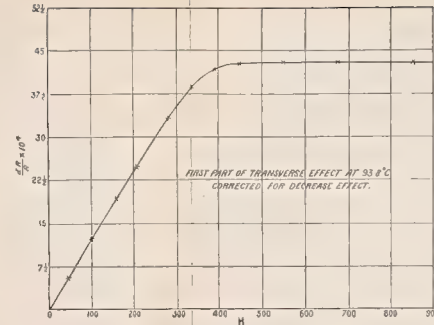


FIG. 9.

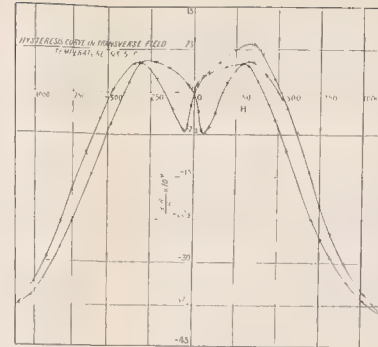


FIG. 11.

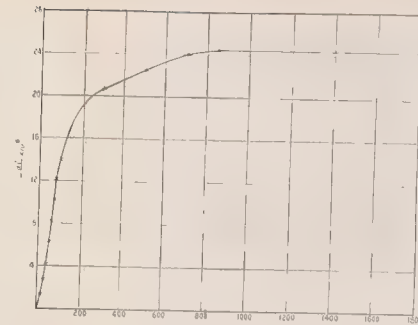


FIG. 2.

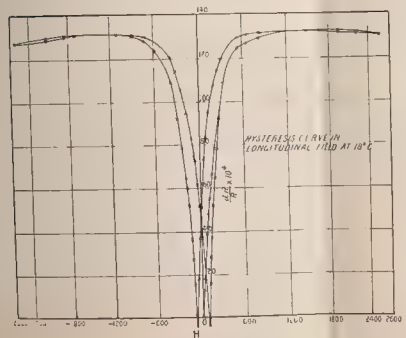


FIG. 4.

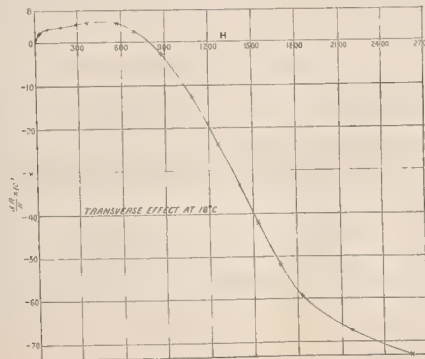


FIG. 6.

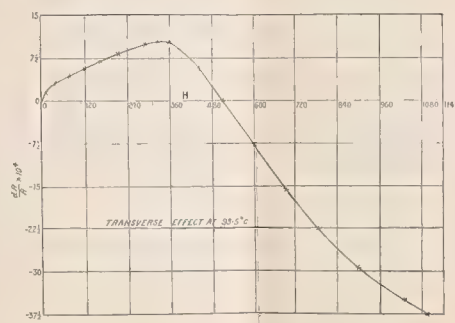


FIG. 8.

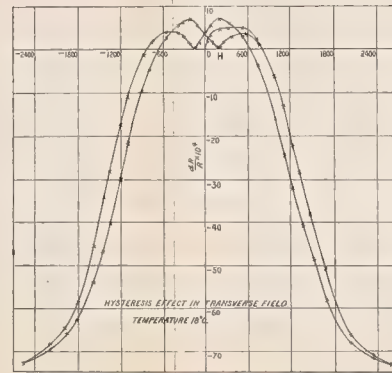


FIG. 10.

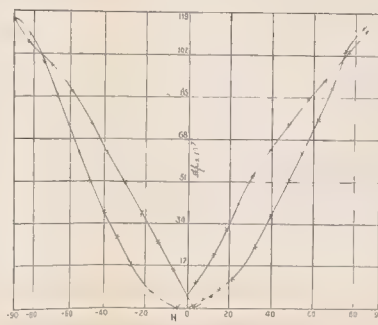
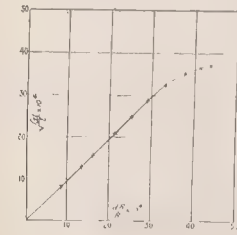


FIG. 12.







THE  
LONDON, EDINBURGH AND DUBLIN  
PHILOSOPHICAL MAGAZINE  
AND  
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

MAY 1914.

LXXXVIII. *The Forces between Atoms and Chemical Affinity.*  
By Sir J. J. THOMSON, O.M., F.R.S.\*

IF the atom is a mixture of negatively electrified corpuscles and positive electricity, it will produce in its neighbourhood a field of electric force. For even when the atom contains equal amounts of positive and negative electricity, the effects of the opposite charges will not wholly counter-balance each other since these charges are in different parts of the atom: there will still be a field of force though the forces will diminish more rapidly than the inverse square of the distance and will also not be uniformly distributed round the atom. These forces will be exerted by the atom not merely on the atoms which are associated with it in the molecule of a chemical compound, but also on the atoms in other molecules, giving rise to forces between the molecules and producing thereby the intrinsic pressure and surface tension of liquids, latent heat of evaporation, cohesion of solids and liquids, the rigidity of solids, and so on. These physical phenomena are the effects of forces between different molecules, whereas chemical affinity and chemical phenomena in general are the effects of forces having the same origin but acting between the atoms in the same molecule.

The consideration of the mutual action between atoms is perhaps the most important part of any atomic theory, for on it depends the explanation of the majority of chemical as well as of physical phenomena.

\* Communicated by the Author.

*Phil. Mag. S. 6. Vol. 27. No. 161. May 1914.*

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Some theories, as for example Laplace's Theory of Capilarity and Boscovich's Theory of the Atom, have attempted to explain many physical phenomena by supposing that the molecules attract each other with forces which are exceeding intense at molecular distance but diminish so rapidly as the distance increases that they very soon become inappreciable. The results obtained by the older and more general theories have been perhaps rather disappointing, and deductions which can be put to the test of experiment would seem more likely to be given by more recent theories, in which the atomic structure of the molecule is brought into prominence, and two atoms of the chemical elements A and B are supposed to exert a force  $C_A C_B \phi(r)$  on each other, where  $C_A$  is a parameter characteristic of the element A,  $C_B$  one characteristic of B, and  $\phi(r)$  is a function of  $r$  the distance between the atoms.

If the forces between the atoms arise from the corpuscles and the positive electricity, they will depend on the orientation of the atoms and will not always be radial; it is only when we take the mean value of these forces that they can be treated as radial and as determined solely by the distance between the atoms.

Sutherland was, I believe, the first to develop a theory of this kind. In a long series of papers in the 'Philosophical Magazine' he worked out the consequences of supposing that the force exerted by an atom was the same as if each atom contained an electrical doublet whose moment was characteristic of the atom; this doublet was carried by the atom unaltered into all the compound molecules of which it formed a part, provided the type of compound remained the same,—it might, however, alter when the type of compound changed. The force exerted between a molecule AB and another CD is equal to

$$(C_A + C_B)(C_C + C_D)\phi(r),$$

where  $C_A, C_B, C_C, C_D$  are the moments of the doublets in the atoms A, B, C, D respectively, and  $\phi(r)$  is proportional to  $1/r^4$  where  $r$  is the distance between the molecules AB, CD. The values of the moments, expressed in electrostatic measures, found by Sutherland for some of the elements are given in the following table\* :—

Element ...	H.	O.	N.	Cl.	Br.	I.
Electrostatic } Moment }	$\cdot 75 \times 10^{-18}$	$1 \cdot 7 \times 10^{-18}$	$1 \cdot 8 \times 10^{-18}$	$4 \cdot 4 \times 10^{-18}$	$5 \times 10^{-18}$	$6 \cdot 2 \times 10^{-18}$

\* "Further Studies on Molecular Forces," Phil. Mag. vol. xxxix. p. 1.

Sutherland found that for the non-metallic elements the electrostatic moment is proportional to the volume of the atom, while for metals the moment is proportional to the linear dimensions of the atom.

The theory is tested by taking some physical quantity, say the magnitude of the surface tension, which can be expressed in terms of the  $C$ 's—the electrostatic moment of the atom—the values of the  $C$ 's for say hydrogen, oxygen, and carbon are found by equating the theoretical value of the surface tension in terms of the  $C$ 's to the observed values in three liquid compounds of these liquids. Having got the  $C$ 's we can calculate the surface tension for as many liquid compounds of these elements as can be obtained, and compare them with the observed values. The agreement, though very far from perfect, is yet good enough to suggest that in many cases the forces around the atom may be represented in this way.

Methods for representing the forces between the atoms have also been developed on somewhat similar lines to this by Einstein \* and also by Kleeman †.

The forces exerted by a molecule  $AB$  can, however, only be represented as the resultant of forces due to doublets of constant moment in  $A$  and  $B$  when both  $A$  and  $B$  are electrically neutral, *i.e.* when neither of them contains an excess of one kind of electricity over that of the opposite. For if one atom  $A$  has an excess of positive electricity, the other  $B$  an excess of negative, the two atoms will give rise to a doublet one of whose poles is on  $A$  while the other is on  $B$ ; the distance between the poles of this doublet, and therefore the force exerted by it, will depend on the distance between the atoms in the molecule. The force will thus depend not merely on the kind of atoms there are in the molecule but also on the way they are arranged, and can not be calculated in the same way as forces due to invariable doublets contained within the atoms themselves. I shall endeavour to show that chemical compounds may be divided into two great classes—in one class the atoms are electrically neutral, in the other they are charged, some positively others negatively,—and that the properties of compounds are strikingly different according as they belong to one class or the other. We might expect that this would be the case, for the poles of the doublet in the compounds of class II. (when the atoms are charged) will be more widely separated than those in compounds of class I., where the two poles of

\* Einstein, *Ann. der Phys.* iv. p. 513 (1901).

† Kleeman, *Phil. Mag.* [6] vol. xviii. p. 491.



any doublet are in the same atom. Thus the moments of the molecular doublets will be greater than those of the atomic ones. We should therefore expect molecules in which the atoms are charged to exert much larger forces on other molecules than molecules in which the atoms are neutral. As large forces between molecules correspond to high intrinsic pressure, surface tension, and dissociating power, we should expect these qualities to be abnormally developed when the atoms are charged.

Let us consider the evidence bearing on the question of electrical charges on the atom.

In my book on 'Rays of Positive Electricity' I have given reasons for thinking that in the molecules of many gases the atoms are not electrified. I will add to these reasons another derived from recent experiments with these rays. On page 94 of 'Positive Rays' attention is called to the fact that a molecule of hydrogen may, after passing through the cathode, split up into two atoms, the energy of the molecule being equally divided between the atoms, so that each has one half the normal amount of energy. They will, therefore, experience twice the electrostatic deflexion of the normal atom and show themselves as a beading at twice the normal distance from the vertical on the parabola representing the hydrogen atom. I have observed similar effects when the gas in the tube was CO: when a molecule of CO splits up after passing through the cathode, the energy of the carbon atom will be  $12/28$ , that of the oxygen atom  $16/28$  of the normal energy; hence the electrostatic deflexion of these atoms will for carbon be  $28/12 = 2.3$ , and for oxygen  $28/16 = 1.7$  times the normal. The beading corresponding to these atoms can be seen in the photographs of the rays through CO, and the deflexions of the beading are as 2.3 to 1.7. Now if the molecule of CO contained a negatively charged oxygen and a positively charged carbon atom, then the oxygen beading would be mainly on the negative parabolas, the carbon beading on the positive one. The photograph shows that the beading occurs on both the positive and negative parabolas of carbon and oxygen, and seems quite as intense on the positive oxygen as on the negative. This result points to the conclusion that in the molecule of CO the atoms are not electrified.

There are thus compounds in which the tendency of the electronegative atom to acquire a corpuscle is not sufficiently powerful to drag a corpuscle from the atom of the electropositive element.

There is, however, evidence from the phenomena of

Positive Rays that in some cases the transference of electricity from one atom in the molecule to the other can take place. For in the Positive Rays we find along with the positively electrified atoms and molecules negatively electrified atoms of such gases as hydrogen, oxygen, carbon, and chlorine, when these gases are in the discharge-tube. These negatively electrified atoms must have been positively electrified at one time or they would not have been driven through the cathode with a high velocity, they must at a later stage have attracted a corpuscle and become electrically neutral, and when in this state, though moving with a high velocity, attracted and retained a corpuscle from the molecules through which they were moving. If they can do this under these unfavourable conditions, it is very improbable that they should not be able when they are in combination with suitable atoms to get a negative charge out of these atoms. Thus we should expect that in the compounds of violently contrasted elements the atoms in the molecule would be charged some with positive, others with negative electricity. We shall see later on direct evidence for the existence of molecules of this type, which I shall call ionic molecules, to distinguish them from molecules in which the atoms are not charged. The process by which the atoms get charged I shall call intra-molecular ionization.

One very direct piece of evidence is given by the value of the specific inductive capacity of compounds, evidence which is particularly strong and easily interpreted when these compounds are gaseous. The setting of the electric doublets under the electric field will contribute to the specific inductive capacity of the gas; hence molecules in which the atoms are charged, since they tend to have abnormally large moments, will also tend to have large specific inductive capacities. Again, since the setting of these doublets involves the rotation of the molecules as a whole, they will move so sluggishly that they are not likely to be affected by vibrations as rapid as those of light-waves in the visible spectrum: hence these doublets will not affect the refractive index in the visible spectrum, while they will affect the specific inductive capacity: we should expect therefore such compounds to depart widely from Maxwell's law that the square of the refractive index is equal to the specific inductive capacity. Again, since the setting of the axes of the doublets under the electric field will be hampered by the collision with other molecules, and as these collisions are more numerous and energetic at high temperatures than at low, the specific inductive capacity of compounds of class II. ought to be

affected by temperature, and to diminish as the temperature increases.

Bädeker (*Zeitschrift für physik. Chemie*, xxxvi. p. 305) has determined the specific inductive capacity of many gases at varying temperatures, and it appears from his results that some of these, such for example as  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{SO}_2$ ,  $\text{HCl}$ ,  $\text{CH}_3\text{OH}$ , &c., exhibit all these characteristics; they have high specific inductive capacities,  $K$  is very much greater than  $n^2$ , and  $K$  diminishes as the temperature increases.

As the specific inductive capacities afford perhaps the most direct way of determining the moments of the electrical doublets in a molecule, we shall proceed to find an expression for the part of the specific inductive capacity due to these moments, using the method employed by Langevin to determine the variation with temperature of the magnetic susceptibility of ferro-magnetic substances.

Suppose that each molecule of a gas contains an electric doublet whose moment is  $M$ , and that the gas is in a uniform electric field, the electric force being  $X$ : when the axis of the doublet makes an angle  $\theta$  with the direction of  $X$ , the potential energy of the doublet in the field will be  $-XM \cos \theta$ : hence the number of molecules in unit volume which have their axes inclined at an angle between  $\theta$  and  $\theta + \delta\theta$  with the direction of the electric force, will be equal to

$$C\epsilon^{hXM \cos \theta} \sin \theta \cdot d\theta,$$

where  $h$  is the constant occurring in Maxwell's law for the distribution of velocities among the molecules of a gas, and  $C$  a quantity which does not depend on  $\theta$ . The moment parallel to the electric force which these molecules contribute is

$$CM \cos \theta \epsilon^{hXM \cos \theta} \sin \theta \cdot d\theta:$$

hence the total moment in the molecules parallel to the electric force is equal to

$$\begin{aligned} & CM \int_0^\pi \cos \theta \epsilon^{hXM \cos \theta} \sin \theta d\theta \\ &= CM \left\{ \frac{\epsilon^{hXM} + \epsilon^{-hXM}}{hXM} + \frac{1}{(hXM)^2} (\epsilon^{hXM} - \epsilon^{-hXM}) \right\}. \end{aligned}$$



But if  $N$  is the number of molecules per unit volume,

$$N = C \int_0^\pi \epsilon^{hXM \cos \theta} \sin \theta d\theta$$

$$= \frac{C}{hXM} \left\{ \epsilon^{hXM} - \epsilon^{-hXM} \right\}.$$

Substituting this value for  $C$  we find that  $P$ , the electrical moment parallel to the electric force per unit volume, is given by the equation

$$P = NM \left\{ \frac{\epsilon^{hXM} + \epsilon^{-hXM}}{\epsilon^{hXM} - \epsilon^{-hXM}} - \frac{1}{hXM} \right\}.$$

The contribution of this to the specific inductive capacity  $K$  is  $\frac{4\pi P}{X}$ ; hence  $K$  will contain the term

$$\frac{4\pi NM}{X} \left\{ \frac{\epsilon^{hXM} + \epsilon^{-hXM}}{\epsilon^{hXM} - \epsilon^{-hXM}} - \frac{1}{hXM} \right\}.$$

Now, except at very low temperatures,  $hXM$  will be an exceedingly small quantity, for  $h$  is inversely proportional to the average kinetic energy possessed by a molecule at the temperature of the gas. At  $0^\circ$  C. this energy is represented by the work done by the atomic charge falling through a potential difference of  $1/30$  of a volt;  $XM$  is this atomic charge multiplied by the potential difference between the poles of a doublet: this, in any feasible electric field, will be exceedingly small compared with  $1/30$ . Hence, unless the absolute temperature of the gas is almost vanishingly small,  $hXM$  is a very small quantity, in this case equation gives

$$K = \frac{4\pi}{3} N h M^2.$$

Now  $h = \frac{1}{RT}$ , where  $T$  is the absolute temperature of the gas and  $R$  is the gas constant  $13.2 \times 10^{-17}$ . Hence these doublets contribute a term

$$\frac{4\pi N M^2}{3RT} = .88 \frac{M^2}{T} \times 10^{36},$$

provided the density of the gas is constant and equal to the density when the temperature is  $0^\circ$  C. and the pressure 760 mm., as in this case  $N = 2.8 \times 10^{19}$ .



Thus  $K$ , the specific inductive capacity of the gas at constant density, may be written

$$K = a + \frac{.88M^2 \times 10^{36}}{T} \dots \dots \dots (1)$$

We shall assume that  $a$  is independent of the temperature, it is probably equal to  $n^2$  where  $n$  is the refractive index. If  $a$  does not depend upon  $T$ , we can find the value of  $M^2$  if we know  $K_1$ ,  $K_2$ , the values of the specific inductive capacity at the temperatures  $T_1$  and  $T_2$ , for from the preceding equation we have

$$K_1 - K_2 = .88 M^2 \times 10^{36} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \dots \dots (2)$$

Bädeker (*loc. cit.*) gives the specific inductive capacity of ammonia gas over a range of temperatures from  $18^\circ.4$  C. to  $108^\circ.4$  C.: from his values I find  $M = 1.5 \times 10^{-18}$  and  $a = 1.00051$ . The experiments on water have a temperature range of only  $8^\circ.6$  C., we cannot therefore expect to get an accurate value of  $M$  for this substance. Substituting the values given by Bädeker, I find for water  $M = 5 \times 10^{-18}$ ,  $a = .939$ . The fact that  $a$  comes out less than unity shows that this value of  $M$  is too large. We shall probably get a more accurate value if we assume that  $K - 1$  for water is due entirely to the doublets in the molecule, and find the value of  $M$  from formula (1) instead of (2): doing this I find  $M = 2.1 \times 10^{-18}$ . Bädeker finds that hydrochloric acid gas, the vapours of methyl and ethyl alcohol and sulphur dioxide all show abnormally high specific inductive capacities: the value of  $M$  for hydrochloric acid is less than that for ammonia, while that of the alcohols is somewhat greater. The molecules of the elements such as  $H_2$ ,  $O_2$ ,  $N_2$ ,  $Cl_2$  give quite normal specific inductive capacities.

Taking as the criterion for the absence of intra-molecular ionization the existence of the relation  $K = n^2$ , where  $K$  is the specific inductive capacity and  $n$  the refractive index, the experiments on the specific inductive capacity of gases show that intra-molecular ionization is absent in the gaseous molecules of the gases in column I., while it is present in those under column II.

I.

$H_2$ .  $CO_2$ .  
 $O_2$ .  $CS_2$ .  
 $N_2$ .  $CCl_4$ .  
 $He$ .  $C_6H_6$ .  
 $Cl_2$ .  $CH_4$ .  
 $CO$ .  $N_2O$ .

II.

$H_2O$ .  $CH_3Cl$ .  
 $NH_3$ .  $CHCl_3$  (slight).  
 $SO_2$ .  
 $HCl$ .  
 $CH_3OH$ .  
 $C_2H_5OH$ .

The values of  $M$  found in this way show that, to separate two molecules in class II., placed so that the axes of their doublets are in the same straight line, will require an amount of work larger than that required to separate the atoms in many chemical compounds. The work required to separate two doublets of the strength of those in the molecule of ammonia, when the distance between their centres is  $10^{-8}$  cm., calculated from the formula  $2M^2/r^3$ , is equal to  $4.5 \times 10^{-12}$  erg. The work required to dissociate a molecule of iodine, as deduced from experiments on the dissociation of iodine vapour, is  $2.3 \times 10^{-12}$  erg. The work required to separate a corpuscle at a distance of  $10^{-8}$  cm. from the centre of the doublet is  $6.7 \times 10^{-12}$  erg, equal to that gained by a fall of the atomic charge through 4.5 volts. This large value explains why gases which show abnormally large values for the specific inductive capacity may be expected to attract to themselves and keep bound any corpuscles in their neighbourhood, and thus, by diminishing the chance of a corpuscle existing in the free state, to diminish the mobility of the negative ions in gases. This effect has long been known to be produced by the vapours of water and alcohol, two gases which Bäckström has shown to possess abnormal specific inductive capacities; it would be an interesting subject for investigation to see whether this property is possessed by all vapours with exceptional specific inductive capacities.

It may be asked why, if the work required to separate two molecules of ammonia is greater than that required to separate two atoms of iodine, is the proportion of free iodine atoms so much smaller than that of free ammonia molecules? The answer to this is found in the consideration of the relative mobility of the systems which exert the attractions in the two cases. If we take two ammonia molecules A and B at random, the force between their doublets is just as likely to be a repulsion as an attraction. In order to develop the maximum attraction the two molecules A and B must wheel round until the axes of their doublets are in the same straight line and point in the same direction: this involves the rotation of two massive molecules. Whereas if we take two iodine atoms C and D and place them at random, all that is necessary to develop their maximum attraction is for the corpuscles inside the atoms to move into new positions; as the inertia of these corpuscles is much less than that of the molecules, the maximum attraction is much more likely to be developed in the case of the iodine atoms than in that of the ammonia molecules, and thus the number

of free iodine atoms may be expected to be much smaller than that of the free ammonia molecules.

Water and the alcohols contain the hydroxyl radicle OH, and the question arises, is the electrostatic doublet whose moment we have been discussing carried by this radicle into the various compounds, and is the intra-molecular dissociation in these practically confined to the charging-up of hydrogen and oxygen atoms in the hydroxyl radicle? If this were the case, then in such compounds, if they were in the gaseous state, the abnormal part of the specific inductive capacity would depend on the number of hydroxyl ions only. Thus, since there are the same number of hydroxyl ions in water, methyl alcohol, and ethyl alcohol, the specific inductive capacities of these in the gaseous state and at the same temperature should be equal. Bädiker's experiments on the vapours of methyl and ethyl alcohols show that these have much the same specific inductive capacities when in the gaseous state, and though water seems to have a somewhat higher value, the difference between them is small compared with that between these substances in the liquid condition. The experiments on vapours are at present not sufficiently numerous to enable us to settle this point, and so we have to turn to the capacities when in the liquid state, though the interpretation of these is much more open to objection. The specific inductive capacity of ethyl alcohol is only 26.8, while that of water is 81. It must be remembered, however, that since the molecule of ethyl alcohol is heavier than that of water, and also because the density of alcohol is less than that of water, there are fewer alcohol molecules per unit volume than there are water molecules.

In the following table I give the values of the quotient of the specific inductive capacities  $K$  of a number of liquids, by the number of the radicles per unit volume; the unit is an arbitrary one:—

#### Radicle OH.

Substance.	K/number of radicles per unit volume.	
	K.	
Water, H.OH.....	81.7	81
Methyl alcohol, CH <sub>3</sub> .OH .....	32.5	79
Ethyl alcohol, C <sub>2</sub> H <sub>5</sub> OH .....	21.7	84
Propyl alcohol, CH <sub>3</sub> CH <sub>2</sub> .CH <sub>2</sub> .OH.	20.5	85 (Thwing)
Glycerine, C <sub>3</sub> H <sub>5</sub> (OH) <sub>3</sub> .....	56.2	76 „



Radicle CN.

Aceto-nitril, $\text{CH}_3\text{CN}$ .....	35·8	100
Proprio-nitril, $\text{C}_2\text{H}_5\text{CN}$ .....	27·2	102
Benzyl cyanide, $\text{C}_6\text{H}_5\text{CH}_2\text{CN}$ .....	16·7	109/ $\delta$ , where $\delta$ is the density
Ethylene cyanide, $(\text{CH}_2)_2(\text{CN})_2$ ...	57·3	127/ $\delta$ [of the liquid.]

Radicle  $\text{NO}_2$ .

Nitromethane, $\text{CH}_3\text{NO}_2$ .....	38·2	116
Nitroethane, $\text{C}_2\text{H}_5\text{NO}_2$ .....	29·5	117

Radicle C.NS.

Methyl rhodanide, $\text{CH}_3\text{CNS}$ .....	35·9	144/ $\delta$
Ethyl rhodanide, $\text{C}_2\text{H}_5\text{CNS}$ .....	26·5	126/ $\delta$

Radicle  $\text{CO-OH}$ .

Formic acid, $\text{HCOOH}$ .....	57	120
Acetic acid, $\text{CH}_3\text{COOH}$ .....	6·46	21
Monochloroacetic acid, $\text{CH}_2\text{ClCOOH}$	20	75
Dichloroacetic acid, $\text{CHCl}_2\text{COOH}$ .	8·22	38
Trichloroacetic acid, $\text{CCl}_3\text{COOH}$ ...	4·55	25

In addition to the electrostatic moment due to the separation of the electrical charges in the doublet itself, there will, since the doublet produces an intense electric field in its immediate neighbourhood, be the electrostatic moment induced by this field in the other atoms of the molecule. This moment will depend on the number and size of these atoms, and will, unless the molecule is unsymmetrical, be in the direction of the moment of the exciting doublet, and will be an invariable companion of this moment. Thus the effective moment of the doublet may be written as  $P + M$ , where  $M$  is the moment of the doublet itself, and  $P$  a quantity which depends on the number and nature of the other atoms in the molecules. The values of the specific inductive capacity for complicated molecules show indications of this effect; for example, the contribution of each doublet of  $\text{OH}$  in benzol alcohol to the specific inductive capacity is considerably higher than the contribution of the same doublet in the simpler molecules of water and methyl alcohol.

Another point that has to be taken into consideration is, that when there are several moment-bearing radicles in the molecule, the axes of these may point so that their resultant is greater than that of any of the constituents, as, for



example, in formic acid,  $\text{H}-\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{OH} \end{array}$ , where each molecule contributes 120 to the specific inductive capacity; glycollic

acid nitrate,  $\begin{array}{c} \text{H} \\ \diagup \\ \text{H}-\text{C} \\ \diagdown \\ \text{H} \end{array} \begin{array}{l} \nearrow \text{OH} \\ \searrow \text{CN} \end{array}$ , where each molecule contributes

215; and formamide,  $\text{H}-\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{NH}_2 \end{array}$ , where each molecule

contributes 210. In other cases the axes of the various doublets might point so that the different doublets opposed each other, and the resultant was less than any constituent.

Acetic acid,  $\begin{array}{c} \text{H} \\ \diagup \\ \text{H}-\text{C} \\ \diagdown \\ \text{H} \end{array} - \text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{OH} \end{array}$ , where each molecule only

contributes 20.2 to the specific inductive capacity, is a conspicuous instance of this effect.

Though there is no intra-molecular ionization in CO, yet when CO enters as a radicle into organic compounds, as in acetone, aldehyde, acetic acid, and similar cases, it acts as a doublet; this would seem to be an example of the effect, alluded to on p. 770, of the presence of other molecules in promoting intra-molecular ionization.

In some molecules only a few of the molecules may be charged, all the others being uncharged. Thus in hydroxyl compounds the atoms in the radicle OH might be the only ones with a charge; in a case like water, however, there are no grounds for supposing that one of the hydrogen atoms is charged and the other uncharged: if both of the atoms have a positive charge, the oxygen atom must have two negative charges and there are in reality two doublets in the molecule.

The hydroxyl radicle OH may exist in the molecule in two states, according as the oxygen atom in it has one or two negative charges. If the oxygen atom has only one charge, then  $\bar{\text{O}}-\overset{+}{\text{H}}$  will form a single doublet, and there need be no other doublet in the molecule. If, however, the oxygen atom has two charges, as presumably it has in a molecule of water, then there must be a positive charge on some atom not in the hydroxyl radicle, and thus there must be at least two doublets in the molecule.

I should like to put forward the suggestion that the difference between these cases from the point of view of

the chemical properties of molecules corresponds to the difference between OH acting as an acid or as a base, and that the acid OH in the molecule is represented by  $\bar{\text{O}}-\overset{+}{\text{H}}$ , while the basic is represented by  $\overset{+}{\text{O}}-\bar{\text{H}}$ .

Consider a molecule  $\text{R}\bar{\text{O}}-\overset{+}{\text{H}}$  in a solution and surrounded by  $\overset{+}{\text{H}}$  and  $\bar{\text{O}}-\overset{+}{\text{H}}$  ions arising from the dissociation of the water; the  $\overset{+}{\text{H}}$  of the molecule would combine with the  $\bar{\text{O}}-\overset{+}{\text{H}}$  ion from the water, and leave therefore an excess of  $\overset{+}{\text{H}}$  ions in the water, and the molecule would therefore have acid properties.

Next consider a molecule  $\text{R}-\bar{\text{O}}-\overset{+}{\text{H}}$  in which the hydroxyl radicle was of the second type: the  $\bar{\text{O}}-\overset{+}{\text{H}}$  in the molecule would combine with the  $\text{H}_+$  ion from the dissociation of the water, would leave therefore an excess of  $\bar{\text{O}}-\overset{+}{\text{H}}$  ions in the water, and therefore the molecule would have a basic character.

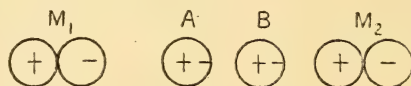
The more electropositive the element R in the molecule ROH, the more likely would there be a transference of a corpuscle from R to O and therefore of O acquiring a second charge, and OH on this view showing basic properties: this is quite in accordance with ordinary chemical experience.

Let us now consider what conditions would have an influence on the process of molecular ionization. We may regard the atoms in the molecules as analogous to an electrical condenser such as a Leyden jar: the work required to charge up such a condenser is, for a given charge, inversely proportional to the capacity of the condenser; hence anything which increases the "capacity" of the molecule will make it easier for the atoms in it to acquire opposite electrical charges. It is by an effect analogous to this that I think the electric field round the molecule can come into play and set at work a mechanism by which the transference of corpuscles from one atom to another in the molecule may be facilitated. Suppose, for example, that A, B represent the atoms in a molecule which when by themselves have so small an electrical capacity that the work required to charge up the one positively, the other negatively, is more than the energy available from their difference in the electro-chemical series. Suppose that there are other molecules in the neighbourhood, and that the electric force

around AB was sufficient to drag some of these molecules up to either A or B or to both of them, producing a more complex system. The proximity of these molecules to A and B would increase the capacity of the system, and would therefore facilitate the passage of a corpuscle from one atom to another, so that these atoms might get charged in presence of these molecules, whereas if they were alone they might remain uncharged.

Another way of considering the effect produced by the other molecules is illustrated by fig. 1. A and B are atoms

Fig. 1.



each containing one corpuscle. The force tending to make the corpuscle in A leave it and pass over to B is the attraction of the doublet in B; the force preventing it is the attraction of the positive charge, which may for simplicity be supposed to act at the centre of A. We see from the figure that when the molecules  $M_1$ ,  $M_2$  containing doublets join on to A and B, their effect is to diminish the attraction holding the corpuscle in A to that atom, and to increase the force tending to pull it out; each of these effects will promote the escape of the corpuscle from A.

A very striking example of the effect of attached molecules in promoting intra-molecular ionization is afforded by the platino-amminio chlorides studied by Werner (Werner's 'New Ideas on Inorganic Chemistry,' English translation, p. 41). The compound  $\text{PtCl}_4(\text{NH}_3)_2$  is not an electrolyte: when, however, another molecule of ammonia is attached, giving the compound  $\text{PtCl}_4(\text{NH}_3)_3$ , it becomes an electrolyte with a molecular conductivity of 96.75; when it takes up another molecule of ammonia and becomes  $\text{PtCl}_4(\text{NH}_3)_4$ , the molecular conductivity rises to 228; while two more molecules of ammonia produce  $\text{PtCl}_4(\text{NH}_3)_6$ , an electrolyte with a molecular conductivity of 522.9. We may regard the acquisition of electrolytic conductivity as evidence that by the addition of ammonia one or more of the chlorine atoms in the salt have been able to attract corpuscles probably from the platinum atom.

Let us first consider the conditions necessary for the occurrence of intra-molecular ionization.

(1) There must be a considerable difference in the electro-chemical properties of the atoms A and B, to furnish the



energy necessary for the transference of a corpuscle from one atom to the other : in other words, A and B must be well separated in the electrochemical series. If the separation is great, the transference of the electricity may take place without the help of other molecules ; but if the intra-molecular ionization has to be brought about by the help of such molecules, then

(2) There must be a strong field of electric force round AB, so as to attract the molecules  $M_1$ ,  $M_2$ . It is not necessary that molecules should attach themselves to both the atoms in AB, although the ionization will occur all the more readily if they do.

(3) The molecules  $M_1$ ,  $M_2$  must be strongly attracted by the field exerted by AB ; thus, if they produce electrical effects analogous to those produced by electric doublets, the moments of these doublets must be large.

We see from this that intra-molecular ionization will only occur in a certain type of molecule, and only molecules with certain properties will be able to produce it.

*Chemical Effects produced by the Electric Fields arising from Intra-molecular Ionization.*

We have seen that the moment of the electrical doublets in the molecules of some gases in which intra-molecular ionization takes place, are so large that the work required to separate two such doublets is quite comparable with that required in some cases to separate the atoms in a molecule. It would seem from this that we might expect that two molecules might, under suitable conditions, be held together by the attraction between two such doublets.

Let us consider the case of a diatomic molecule AB held together, either by the forces exerted by the intra-atomic doublets in A and B respectively, or by these in addition to the forces between the charges on A and B when intra-molecular ionization has taken place ; we need not for the moment distinguish between these cases. Outside the molecule there will be a stray electric field, whose magnitude will depend largely upon the nature of the atoms A and B. The stray field will not be so intense as that between the atoms, and so might be unable to bind another atom in which there are only intra-atomic doublets which are necessarily of small moment, as there is no room inside the atom for a wide separation of the poles of the doublet. Again, any compound with an atom would be "unsaturated"; thus the kind of combination we are considering will be between molecules, and not between atoms.



If, however, instead of an atom we had a molecule in which there was intra-molecular ionization, its moment would be far larger than that of the atom, and it would be attracted by the field of force round AB with much greater intensity. The force might be large enough to bind the molecule to AB, and we should have a system represented by AB—M. Thus molecules like those of water, ammonia, alcohol, sulphur trioxide, which have large electrical moments, might be expected to enter into combinations of this kind, forming complexes of two or more molecules. This is the type of compound called by chemists molecular compounds, and which at one time were often called into requisition to explain the existence of compounds which did not follow the law of constant valency. Of late, however, the idea of molecular compounds seems to have gone out of favour.

It seems to me that when we take into consideration the strength of the electric field exerted by some molecules, it is very difficult to believe that molecular compounds are not formed, and that they do not play a large part in many chemical reactions. We have seen (p. 770) that union with another molecule promotes intra-molecular ionization; thus it might happen that the atoms in AB were uncharged when AB was isolated, but when it had attracted another molecule a corpuscle would pass between A and B so that these atoms would get charged. In this way the properties of AB might be entirely changed by union with another molecule. We can, I think, go further than this. May there not be cases in which the attached molecule or molecules act on AB in much the same way as the molecules of a solvent would act upon it in solution, so that the atoms of A and B, in addition to getting charged through the proximity of the molecules attached to AB, might get separated by a kind of intra-molecular dissociation, and then rearrange themselves so as to be in equilibrium with the atom of M, the molecule attached to AB.

To take the most famous case in connexion with the formation of molecular compounds, that of sal-ammoniac. We may regard this as produced by a molecule of ammonia, which as we have seen has an exceedingly large electrostatic moment, being attracted by the electric field round the molecule of hydrochloric acid. This is only the first stage: may not the HCl, under the action of the molecule of ammonia, not merely have the H atom positively, the Cl atom negatively electrified, but the two torn apart from each other? The four H atoms, and the N and Cl atoms might then regroup themselves so as to be in equilibrium. If this took

place, the result of the union of the ammonia and hydrochloric acid could not be correctly represented by the formula  $\text{NH}_3\text{—HCl}$ .

As Professor Baker has shown, the union of ammonia and hydrochloric acid does not take place if the gases are dried with extreme care. We can, I think, see a reason for this, if we regard the forces which primarily bring the molecules of the ammonia and hydrochloric acid together as due to electrostatic doublets in the molecule. These forces are essentially polar in their nature and depend to a very large extent on the angle between the axes of the two doublets when the molecules come close together; the attraction is large only when the angle between these axes is small. Thus, when the molecules of the two gases come into collision, it will be only in a very small fraction of the collisions that the circumstances are favourable to the union of the molecules. If, however, there are nuclei present, such as minute drops of water, then some of the molecules of the gases will, as it were, be anchored round the nuclei: thus a molecule of  $\text{NH}_3$  and one of  $\text{HCl}$  will be kept close together for a considerable time; this will enable the molecules to arrange themselves under the forces they exert on each other, and they will tend to set so that the axes of the doublets come nearly into line; the molecules in this position will exert the maximum attraction on each other, and thus be in the condition most favourable for combination.

A molecule of gas with a large electrostatic moment may itself promote combination between two gases in whose molecules there is no intra-molecular ionization. Let us consider the effect of a molecule of this kind on the molecules of the gas round it. The intense electric field round this molecule will drag towards it the molecules around it, so that it will act as a nucleus round which the molecules of the other gases condense. This nucleus will thus bring these molecules closer together than they otherwise would be, and if, like chlorine and hydrogen, they can combine, the presence of the nucleus will assist combination. It seems possible that part of the effect of water-vapour may arise from an action of this kind, the interacting molecules crowding together so as to get into the strongest part of the electric field round the water molecule, and thus getting into positions which are favourable for chemical combination.

In some cases the product of the chemical action will be active molecules with large moments; this will happen in the case of hydrogen and oxygen, and again with hydrogen and chlorine, as the molecules of water and hydrochloric

acid are of the type in which there is intra-molecular ionization. In cases like these the further chemical combination goes on the greater will be the number of the nuclei which promote the combination; there will evidently be a tendency for reactions of this type to become explosive.

The condensation of the gas round a molecular doublet such as occurs in water is, on this view, due to the strong electric force round the doublet. If instead of a molecule with its doublet we had a charged ion, we should have a still stronger field and still more condensation. The Conduction of Electricity through Gases gives us evidence of such condensation, as the ions behave rather as if they were clusters of molecules than simple molecules or atoms. It may, however, be asked why is it, if the molecular doublets are able to accelerate chemical actions, that the speed of such reactions is not notably greater in an ionized gas than in one which is not ionized? The answer is that in any ordinary type of ionization the number of charged ions is exceedingly small in comparison with the number of molecules of a substance, even when this is present as the merest trace. Take, for example, the case of water-vapour: if the partial pressure of the vapour were only the millionth of an atmosphere, there would still be about  $2.8 \times 10^{13}$  molecules of water-vapour per cubic centimetre. It would be exceptionally strong ionization by such an agent as Röntgen rays to produce  $10^{10}$  ions per cubic centimetre, so that the molecules of water-vapour when this trace of water was present would be about three thousand times the number of ions. In cases where there are exceptionally large numbers of ions present, as for example in the negative glow in a discharge-tube, all kinds of chemical action seem to go on with great facility.

*On the Number of Active Molecules which a Molecule of a different kind can hold in Combination.*

We shall denote one of the active molecules by B, the molecules to which these are attached by A. We have to consider in the first place whether A can hold even one of the type B bound. From general Thermodynamical considerations it is clear that the system AB will not be formed in appreciable quantities unless the work required to separate A and B when they are in combination is considerably larger than  $R\theta$ , the energy corresponding to one degree of freedom at the absolute temperature  $\theta$ . If we regard the electric field round the atoms as equivalent to those produced by electrical doublets whose moments are respectively M, M',



the work required to separate the constituents will be equal to  $2MM'/d^3$ , where  $d$  is the distance between the centres of the doublets. Now we may take  $d$  as comparable with  $10^{-8}$  cm. and put  $d = x \times 10^{-8}$  cm., and from the values given on page 764  $M$  and  $M'$  are comparable with  $10^{-18}$ , and are say  $y \times 10^{-18}$ ,  $z \times 10^{-18}$  respectively. The values found for  $M$  and  $M'$  show that  $y$  and  $z$  will be small compared with unity except for molecules in which there is intramolecular ionization, and even then they will not be large, as the largest value we found was that for water, where  $M = 2.1 \times 10^{-18}$ . Expressed in terms of  $x$ ,  $y$ ,  $z$ , the work  $2MM'/d^3$  required to separate A and B is equal to  $\frac{2yz}{x^2} \times 10^{-12}$

erg. The work required to separate the atoms in a molecule of iodine is about  $2 \times 10^{-12}$  erg, and this molecule is dissociated to a very considerable extent at temperatures of  $300^\circ$  or  $400^\circ$  C. It follows from this that if  $yz/x^2$  were as small, say, as  $1/10$ , the compound AB would be almost wholly dissociated at ordinary temperatures; for this compound to exist then  $yz/x^2$  must not be a small fraction. With moments each as large as that in the ammonia molecule, this condition is fulfilled, but it is evident from the numbers that there is not any very great margin; and if one of the moments fell to as small a value as we might expect when there is no molecular ionization, it would only be in cases where  $x$  is exceptionally small that we could expect the compound to exist at ordinary temperatures. The study of the magnitudes involved thus leads us to the conclusion that though this molecular combination may occur not infrequently, it will be by no means universal and will probably be limited to special types of molecules. Let us suppose, however, that this condition is fulfilled, and that a compound AB can exist: what are the prospects of A being able to hold a second molecule of B in combination? It is clear that the first molecule will have taken up the strongest part of the electric field round A; if a second molecule B moves up to A, it has to take up a position where the attraction which binds it to A is less intense than that which bound the first molecule; and, moreover, since the doublets in the two molecules of B will repel each other, the one first in the field will be driven from its specially favourable position, so that when the two molecules of B are present in the compound  $AB_2$ , neither is attracted to A quite so strongly as the single molecule B in the compound AB. Similar remarks will apply when a third molecule B is added to form the compound  $AB_3$ ; in this case none of the B molecules will be held quite as firmly as in



either of the compounds  $AB$  or  $AB_2$ . The attachment of the  $B$  molecules will get looser and looser as successive molecules of  $B$  are added, until finally we reach  $AB_n$ , in which the work required to detach a  $B$  molecule becomes comparable with the energy corresponding to one degree of freedom at the temperature of the compound. This compound  $AB_n$  will be unstable, or rather will not exist in appreciable quantities, so that the compound  $AB_{n-1}$  will be the one richest in  $B$  that can be detected. There will thus be a definite limit to the number of  $B$ 's that can be bound to the  $A$  molecule, and we should expect from the values found for the moments of the electrostatic doublets in the cases where we have the data for calculating them, that this number would not be large. Water of crystallization is a case of this kind,  $B$  representing the water molecule; in general the number of molecules of water of crystallization is not large. If the molecule  $A$  contained several atoms, there might be several regions where the molecules  $B$  might find a place. If  $A$ , for example, contained two atoms,  $\alpha$  and  $\beta$ , and the electric fields round  $\alpha$  and  $\beta$  were equal in intensity, then if the field round  $M$  were symmetrical we might have molecules of  $B$  attached to  $\alpha$  and  $\beta$  as in the scheme



More molecules of  $B$  might be added if the fields due to  $\alpha$  and  $\beta$  were strong enough, some to the left, an equal number to the right, so that the  $B$  molecules in a compound of this type would be done up into two bunches. If the molecule  $A$  had a more complex structure, there might be more than two different regions in which the  $B$  molecules could group themselves, so that the  $B$  molecules attached to an  $A$  molecule might be divided into more than two groups. We see in this way that the number of water molecules which are able to exist in any one group may be considerably less than the number of molecules of the water of crystallization.

The electrostatic effect of a doublet at a considerable distance from its centre depends only on the moment,—the product of either charge and the distance between the two charges. At close quarters, however, other things may come into consideration; for example, if we compare the charged atoms in the doublet to two charged spheres, the moment at a considerable distance is independent of the radii of these spheres if the distance between their centres remains constant. Close up to these spheres, however, the electric force will depend upon their radii, and will be greater at the surface

of the smaller sphere than at that of the larger one. In a case like this the field due to the molecule may be unsymmetrical and the molecules *M* may attach themselves to one side of *A* rather than to the other; we may express this by saying that one atom in the molecule *A* can form these molecular complexes while the other can not. In the illustration given above we have supposed that the lack of symmetry is due to the difference in size of the atoms in the molecule *A*. Although the meaning we attach to the idea of atomic volume depends to a large extent on the view we take of the constitution of the atom, yet on almost any view the electric force at the surface of a charged atom would be larger for an atom with a small "volume" than for one with a larger one. We may see an illustration of this in the case of the alkali metals. These can lose a negative corpuscle with exceptional ease, which may be taken as an indication that the force exerted by a positively charged atom on a corpuscle at the surface of the atom is exceptionally small. Now the atoms of the alkali metals are distinguished for their large atomic volumes, and their electropositive character increases from lithium to cæsium along with their atomic volumes. We should thus expect that, at any rate with elements of the same type, those with a small atomic volume would be more likely to form molecular complexes than those with larger; that, for example, lithium would be more likely to form molecular compounds than cæsium. The fact that of the chlorides of the alkali metals lithium chloride is the most deliquescent, may be an example of this effect.

Any want of symmetry in the *B* molecules may result in their attaching themselves to one of the atoms in the *A* molecule in preference to the other: thus, if in the electrostatic doublet in the *B* molecule the electric force close to the negative end of the doublet is greater than that close to the positive end, *B* will tend to attach itself to the atom in *A* which has the positive charge, when there is intra-molecular ionization in *A*; while if the force close to the positive end of *B* was greater than that close to the negative, *B* would attach itself to the other atom in *A*. We thus see that the atoms in a molecule *A* to which other molecules are linked will depend on the nature of *B* as well as on that of *A*. And it does not follow because water of hydration is linked to one atom in a molecule of *A*, that the molecules of all the other substances which show intra-molecular ionization—ammonia, alcohol, hydrochloric acid and the like—will necessarily be linked to the same atom.

The formation of these molecular compounds would

naturally be more likely to take place if both A and B were active molecules, *i. e.* if both had exceptionally large electrostatic moments. There may, however, be cases in which there is combination, though only one of the molecules, B is of this type. From what we have pointed out on page 770, the approach of B to A will promote the charging up of the atoms in the molecule A, even if they were not charged originally, and thus tend to bring A into the active state even if it were not in that state before its union with B.

We can readily understand why liquids whose molecules have large electric moments should be able to produce great ionization when electrolytes are dissolved in them. For in the first place the molecules of the solvent attach themselves to the molecules of the electrolyte, attract them and thus tend to pull the atoms apart. Secondly, the large electric moment of the molecules will cause the solvent to have a very high specific inductive capacity, so that when the oppositely charged atoms of the electrolyte are once separated, the attraction between them will be diminished; this diminution in the attraction will diminish their rate of recombination. Since  $n$  the number of free ions per cubic centimetre is

proportional to  $\epsilon^{-\frac{w}{2R\theta}}$ , where  $w$  is the work gained by the recombination of the ions,  $\theta$  the absolute temperature and  $R$  the gas constant, we see by putting  $w = w_0/K$ , where  $w_0$  is the work gained when the ions recombine in a medium whose specific inductive capacity is unity, and  $K$  is the specific inductive capacity of the solvent, that  $n$  will be proportional

to  $e^{-\frac{w_0}{2RK\theta}}$ ; thus when  $w_0$  is large compared with  $R\theta$ ,  $n$  will increase with great rapidity with any increase in  $K$ . Examples of this effect are to be found in the extremely interesting and important series of investigations on the influence of specific inductive capacity on ionization by Walden in a long series of investigations published in the *Zeitschrift für Phys. Chem.*

The following table is taken from his paper "Organische Lösung- und Ionisierungsmittel," *Zeits. für Phys. Chem.* liv. p. 129.  $K$  is the dielectric constant of the solvent,  $v$  the dilution required to produce a dissociation of 83 per cent. in a solution of  $N(C_2H_5)_4I$ .

Another physical property which differentiates the compounds with uncharged atoms from those with charged, is that known as electrification by bubbling. When air and other gas bubble through a liquid, such as water, alcohol, acetone, in which there is intra-molecular ionization, the gas



Solvent.	K.	v.
H <sub>2</sub> O .....	80	32
CH <sub>3</sub> NO <sub>2</sub> .....	40	200
C <sub>5</sub> H <sub>4</sub> O <sub>2</sub> .....	39	200
CH <sub>3</sub> CN .....	36	320
CH <sub>3</sub> SCN .....	36	270
CH <sub>3</sub> OH .....	32.5	400
C <sub>2</sub> H <sub>5</sub> CN .....	27.2	800
C <sub>5</sub> H <sub>8</sub> O <sub>2</sub> ..	26	1000
C <sub>4</sub> H <sub>6</sub> O <sub>3</sub> .....	17.9	2000
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CN.....	16.7	3200

when it emerges is mixed with positive and negative ions; little if any electrification, however, is found when the gas bubbles through a liquid like paraffin oil or benzene where the atoms in the molecule are not charged. This is shown very clearly by the recent experiments of M. Bloch, *Annalen de Chim. et de Physique*, xxiii. p. 28 (1911).

We could account for this difference in the following way. When the gas bubbles through the liquid fresh liquid surfaces are continually being produced; these surfaces have an amount of energy equal per unit area to the surface tension. Since this energy tends to a minimum, the effect of the action between the molecules which produces surface tension will be to promote any change which diminishes the surface tension at the fresh surface. For example, if any chemical action will diminish the surface tension, that action will take place more readily at the fresh surface than in the body of the liquid. If the liquid is a salt solution, the salts will flock to the surface if the surface tension of a strong solution is less than that of a weak one and recede from it if it is greater. If two isomeric compounds have different surface tensions, then spraying or bubbling air through a mixture will increase the proportion of the one with the smaller surface tension. The molecules of a compound AB might split up at the surface layer into atoms, if a layer of dissociated atoms either mixed together or in separate layers would give a smaller surface tension than the undissociated liquid.

We see from this that the causes which produce surface tension might dissociate the molecules of the liquid at the surface of the cavities formed by the bubbling of the gas through the liquid. If the liquid were of the type in which



there is no charge on the atoms, the dissociation would not give rise to charged ions which could be carried along by the gas, but if the atoms in the molecule were charged the dissociation would produce ions, and these being carried along by the gas would produce electrification like that observed when gas bubbles through these liquids.

The magnitude of the electrification is of the same order whether the liquid through which the gas is bubbled is distilled water or a salt or acid solution, though there are in other respects very marked differences between the two cases. As the number of ions in the solution is of quite a different order from that in the water, we conclude that the electrification cannot be due to the unaided diffusion of these ions into the cavities produced by the air-bubbles.

*On the conditions for the existence of a Chemical Compound and on Valency.*

In order that a chemical compound may exist in a stable form it must satisfy certain conditions: one of these is that its molecules must not exert on other molecules in their neighbourhood attractions large enough to cause the molecules to unite and thus form other systems; another condition is that the attractions between the atoms in the molecule must be great enough to hold them together in spite of the blows they receive when the molecule collides with other molecules. It depends to a very large extent on the temperature whether these conditions are fulfilled or not. The first condition will be satisfied if the work required to separate the two molecules whose combination is under consideration is small compared with  $\alpha \theta$ , the energy corresponding to one degree of freedom at  $\theta$ , the absolute temperature of the molecules. The second, if the work required to separate the atoms in the molecule is large compared with the same quantity. Thus at high temperatures we may have systems existing in a stable form which would pass into more complex ones if the temperature were lower, while on the other hand some molecules would break up at high temperatures though they would be stable at lower ones. Both these conditions are illustrated by a case like that of iodine vapour, whose molecules at a high temperature are monatomic while at a lower one they are diatomic. Thus the question as to whether a substance is, or is not, 'saturated,' involves essentially the question of temperature, and even unsaturated substances can exist if the temperature is not too low.

If we take the view that the forces exerted by the atoms are due to charges of positive and negative electricity, the negative electricity being on the corpuscles, then the force exerted by an atom in the region around it will depend mainly upon the mobility of its corpuscles.

For if an atom A has some corpuscles which can move freely about in the atom, then, if an electrical system of any kind is brought into the neighbourhood of A, these corpuscles will move into such a position that there will be attraction between A and the system. For example, if A contained a single free corpuscle and the system B were an electrical doublet, the corpuscle would move into such a position as to attract the doublet in whatever position that might be placed, and as the corpuscle is extremely mobile this shift can take place with great facility.

If, however, the corpuscles were fixed in the atom, then if it were not in such a position as to attract B originally (and it is just as likely to be in a position to repel as to attract), in order to attract it, the whole atom A, whose mass is very much greater than that of a corpuscle, would have to wheel round, and this on account of the much greater inertia of the atom would be a matter of much greater difficulty than the motion of the corpuscle in the former case.

Thus we may regard an atom all of whose corpuscles are fixed as incapable of exerting any great attraction on other atoms around it unless these are in particular positions, we shall suppose that an atom in this state is what the chemists call saturated. So that our criterion of saturation will be that all the corpuscles in the atom are held fast by the forces acting upon them.

We regard the negatively electrified corpuscles in an atom as arranged in a series of consecutive layers; those in the inner layers we suppose are so firmly fixed that they do not adjust themselves so as to cause the atom to attract other atoms in its neighbourhood. There may, however, be a ring of corpuscles near the surface of the atom which are mobile and which have to be fixed if the atom is to be saturated. We suppose, moreover, that the number of corpuscles of this kind may be anything from 0 to 8, but that when the number reaches 8 the ring is so stable that the corpuscles are no longer mobile and the atom is so to speak self-saturated.

The number of these mobile corpuscles in an atom of an element is equal to the number of the group in which the element is placed on Mendeleef's arrangement.

Thus helium and neon have no free corpuscles; hydrogen,

lithium, sodium, potassium, each 1; beryllium, magnesium, calcium, and strontium, 2; boron, aluminium, 3; carbon and silicon, 4; nitrogen, phosphorus, and arsenic, 5; oxygen, sulphur, and selenium, 6; fluorine, chlorine, bromine, and iodine, 7.

Now let us consider how the corpuscles in these atoms can be fixed. They are not fixed when the atom is by itself. In this case the tube of force starting from a corpuscle in the atom, returns to a positive charge in the same atom and possesses considerable mobility, as the corpuscle at one end of it can move freely about in the atom. The corpuscle will not be fixed unless the tube of force at its end is anchored to something not in the atom, *i. e.* it must end on another atom. Thus if there are  $n$  free corpuscles in the atom, to fix these and thus saturate the atom, the  $n$  tubes of force which start from the  $n$  corpuscles must all end on other atoms and not return to the original atom. Thus to ensure saturation from every free corpuscle in an atom, a tube of force must pass out of that atom and end on some other, and this must hold for every atom in the molecule. When the atoms are electrically neutral, *i. e.* have no excess of positive over negative charge or *vice-versâ*, for each tube of force which passes out of an atom, another must come in; and thus each atom containing  $n$  corpuscles must be the origin of  $n$  tubes going to other atoms and also the termination of  $n$  tubes coming from other atoms.

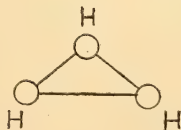
Thus consider two atoms A and B each of which contains one free corpuscle, denote these corpuscles by  $\alpha$  and  $\beta$  respectively. Then  $\alpha$  and  $\beta$  will be fixed if a tube of force goes from  $\alpha$  in A to the positive core of B and another from  $\beta$  to the positive core of A: in this case the molecule AB will be saturated. If, however, B had contained two mobile corpuscles  $\beta$  and  $\gamma$ , then, though  $\alpha$  might be fixed by a tube going from it to the core of B, yet since only one tube goes out of A only one can come in; thus only the tube from one of the corpuscles in B can go to A; the tube from the other must return to B, and thus this corpuscle will not be fixed and B will not be saturated. If, however, there is a second atom of A in the neighbourhood or any other atom C which contains only one free corpuscle, then this tube of force from  $\gamma$  can go to the positive core of C while the tube from the corpuscle in C comes to the core of B. With this arrangement every mobile corpuscle in the system is anchored by a tube of force to some other atom, and thus deprived of mobility: hence the system will be saturated.



We may in a diagram represent the tubes of force proceeding from a corpuscle in an atom by a straight line drawn from the symbol representing the atom, and we see that the condition that all the atoms in the molecule should be saturated is that we should be able to draw a diagram so that the symbol which represents any atom which contains  $n$  free corpuscles should be the origin of  $n$  of these lines going to the symbols representing other atoms, and the termination of an equal number coming from other atoms.

If we take the structural formula of any valency compound as represented in the usual way by bonds between the atoms, and double each of the lines representing a bond, then we may regard one of these lines as representing a tube of force going from the atom and the other a tube entering the atom; and inasmuch as in the diagram of a valency compound the symbol representing an atom of valency  $n$  is connected with  $n$  of these bonds, we see that the condition given above for saturation will be fulfilled. Thus every compound which satisfies the usual conditions for valency will also satisfy the conditions of our theory. It must be noticed, however, that the conditions of the ordinary theory are more stringent than the new one, and that many compounds satisfy the new conditions of valency which do not satisfy the old. When we doubled the lines representing the bonds in the usual structural formula and took one of these lines to represent a tube going from the atom and the other one coming to it, we practically only included the case when if an atom A sends a tube to another B, it receives in return one from the same atom; this on our view is not necessary: all that is necessary is that the number of tubes which leave A should equal the number which enter it. It is not necessary that the atoms from which A receives the tubes should be the same as those to which it sends them.

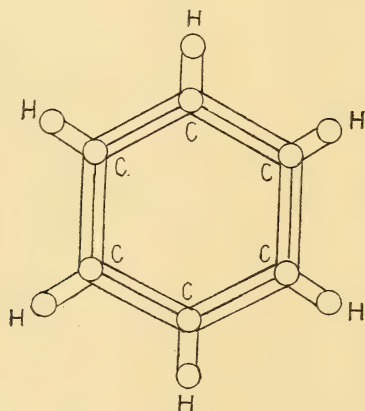
An example or two may make this clearer. On the new view  $H_3$  is a possible valency compound, even when hydrogen is monovalent, as the following diagram shows. Each atom



in  $H_3$  is the origin and also the termination of a tube of

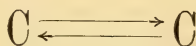


force which, since the hydrogen atom only contains one free corpuscle, is the only condition that has to be fulfilled. On the usual theory of valency,  $H_3$  is not possible as a valency compound. Again, taking silver as monatomic,  $Ag Cl$ ,  $Ag Cl_2$ , or indeed  $Ag Cl_n$  would all be possible valency compounds, though they would not on the older theory. The difference between the two theories is specially noticeable in the case of ring or chain compounds, and it is interesting to write down the simplest formula for benzene from this point of view ; it is

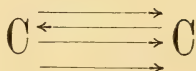


It will be seen that this benzene ring is entirely symmetrical, and that the linkage between the carbon atoms is not the same as that in

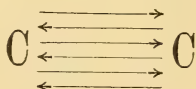
ethane



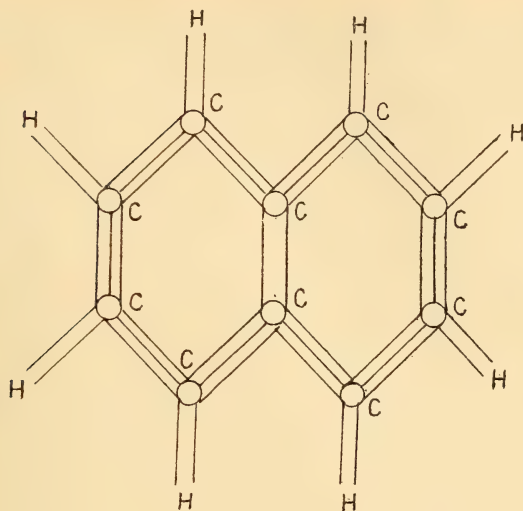
ethylene



or acetylene



while naphthalene can be represented as



This formula, like that for benzene, is quite symmetrical, and all the affinities are provided for.

The difference between the theory we are considering and the accepted theory of valency may be expressed by saying that not only is every possible valency compound on the old theory a valency compound on this theory, but every compound which would be a valency one on the old theory if the valency of every element was doubled, *i. e.* if hydrogen were regarded as a dyad, oxygen as a tetrad, nitrogen as a hexad, and so on, would be a valency compound on the new, with the atoms retaining their original valency. This only applies to the compounds when the atoms are uncharged; when the atoms are charged the valency conditions are, as we shall see, the same as on the old theory.

The distribution of electricity on the atoms in the cases we have been considering, corresponds to tubes of force going from a corpuscle near the surface of one atom to the core of another. It corresponds, for the case of two atoms each containing a single corpuscle, say two atoms of hydrogen, to that represented diagrammatically in fig. 2. We see that in this case the shortest distance between oppositely charged particles is considerably greater than the minimum distance

between the surfaces of the atoms. We call this type of distribution that corresponding to the exertion of positive valency.

We have supposed, however, that a ring of eight corpuscles is a rigid system, and one therefore that does not require any anchoring of its corpuscles to become saturated. Now we can regard a ring of seven as a ring of eight, minus one corpuscle; and as the absence of a negative charge is equivalent, as far as the electric force is concerned, to the presence of a positive one, the ring of seven corpuscles may be regarded as a ring of eight plus a positive charge. The ring of eight will saturate itself, while to fix the positive charge we only require one tube of force. Thus, when looked at from this point of view, the valency of the atom is only one, while from the other way of looking at it the valency was seven. In the one case, however, the electrical doublet which represents the electrical field due to the atom has the positive pole near the surface, the negative near the core; while, as we have seen, in the original way of considering the question the equivalent doublet had its negative pole near the surface and its positive one close to the centre. In the case where the corpuscles are arranged so that the positive pole of the doublet is nearer the surface than the negative, we shall regard the atom as exerting an electronegative valency. Again, a ring of six corpuscles may be regarded as a ring of eight corpuscles and two positive charges, and thus as having an electronegative valency equal to two.

Thus we see that an atom may exert an electropositive valency equal to the number of mobile corpuscles in the atom, or an electronegative valency equal to the difference between eight and this number. Each atom can, in fact, exert either an electropositive or an electronegative valency, and the sum of these two valencies is equal to eight. In this respect the theory agrees with Abegg's theory of positive and negative valency. There is, however, this difference between them, that on Abegg's theory the atom can bring both sets of valencies into play at the same time, while on the view we are discussing the atom can exert one or other of these valencies, but not both simultaneously. It is possible that the number of corpuscles which form a rigid ring may depend to some extent on the number of corpuscles in the inner rings, *i. e.* on the atomic weight of the elements, and that for elements with atomic weights greater

than forty this number may not be eight; if this should prove to be the case, the sum of the positive and negative valencies for such elements would not be equal to eight.

The union between two atoms exerting opposite valencies might be expected to be firmer in general than that between atoms exerting valencies of the same kind. For when they are exerting valencies of the same sign, the electric doublets which represent the forces between the atoms are arranged

Fig. 2.



as in fig. 2; whereas when they are exerting valencies of opposite signs they will be arranged as in fig. 3. It will be

Fig. 3.



seen that if the distances between the centres of the atoms are the same in the two cases, the forces between the doublets will be greater in the case represented by fig. 2 than in that represented by fig. 3, as the opposite poles of the two doublets are much nearer together in the first than in the second case.

If the forces between the atoms were sufficiently large to drag the corpuscles out of the electropositive atom and heap them on to the electronegative one, we see that after the transference had taken place there would be no mobile corpuscles left on the electropositive atom; and as the number of corpuscles in the outer ring of the electronegative element would be increased to eight, and eight forms a rigid ring, there would be no mobile corpuscles on the electronegative atom either.

When the corpuscles are transferred from one atom to another there is a diminution in the number of tubes of force, and if all the mobile corpuscles are removed from the



electropositive elements the number of tubes of force will be halved. We can easily see this, because when the corpuscles leave the atoms they carry with them all the tubes of force which left the atom; thus, while before the transference of the corpuscles took place there were as many tubes entering each atom as leaving it, after the transference no tubes will leave the electropositive atom and none enter the electronegative ones. The number of tubes will thus be halved. And in this case we can easily see that they are represented by the symbols representing the bonds on the usual valency theory. Thus, when there is intra-molecular ionization, we see that our theory leads to the same condition for saturation as the usual one. We have seen, however, that when there is no transference of corpuscles there is a difference between the theories, and many compounds are valency ones on the new theory, though they are not so on the old.

From this point of view compounds are to be divided into two types according as their molecules do or do not contain charged atoms. The valency considerations for compounds of the second type are more elastic than for those of the first, inasmuch as an atom when it occurs in a compound of the second type may be regarded as having twice as many bonds as when it occurs in a compound of the first type, the number of bonds in this type of compound being the same as that on the usual theory of valency.

The compounds which are compatible with this theory of valency, but incompatible with the old, will be mainly ring or long chain compounds, and so are unlikely, unless they contain carbon atoms, to have any great stability. It must be remembered that fulfilment of valency conditions does not ensure stability or the possibility of existence under ordinary circumstances; other conditions have to be satisfied for this to be possible.

The view we have taken of saturation is that when each of the mobile compounds in an atom is anchored by a tube of force passing to a neighbouring atom, the average attraction of the atom on other atoms is reduced to a minimum. It must, however, be remembered that in consequence of the dissociating effects due to heat, molecules can exist in a free state at a temperature  $\theta$  when the work required to separate an atom from the molecule is not considerable in comparison with the average kinetic energy of the molecule at the temperature  $\theta$ . The existence of unsaturated compounds is thus what we should expect from thermodynamical considerations.

The real difficulty is not to explain why some unsaturated compounds exist, but why others of analogous chemical constitution are not found in the free state. Thus, for example, it is not so much the existence of CO that requires explanation as the fact that while in this compound the carbon atom exerts so little attraction on another carbon atom that the compound  $O=C=C=O$  is not found, in  $CH_2$  the carbon atoms have so much affinity for other carbon atoms that  $CH_2$  does not under ordinary circumstances exist in a free state (though it is found in vacuum tubes) but at once unites to form the compound  $C_2H_4$ . Or, to take a case still more analogous, since in CO the carbon is combined with a more electronegative element, why is not  $CCl_2$  found in a free state?

I think we can see a reason for this difference, if we remember that each atom even when saturated produces a strong electric field in its neighbourhood, and that this field will tend to restrict the freedom of motion of the corpuscles in a neighbouring atom. Thus, if the electric field due to the oxygen atom in CO were very strong, then though only two out of the four mobile corpuscles in the carbon atom are bound by tubes of force to the oxygen atom, the other two would be exposed to a strong electric field and would have their mobility thereby reduced, and in consequence the attraction of the carbon atom on other atoms would be diminished. The diminution in the attraction would depend upon the strength of the electric field in the carbon atom due to the oxygen atom. If the field exerted by the two hydrogen atoms in  $CH_2$ , or the two chlorine atoms in  $CCl_2$ , were smaller than that exerted by the oxygen atom in CO, then the carbon atom in CO would be much more nearly saturated than the ones in  $CH_2$  or  $CCl_2$ , and so the former molecule might exist in a free state while the others could not.

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LXXXIX. *The Discharge of Electricity from Cylinders and Points.* By Professor J. S. TOWNSEND, M.A., *New College, Oxford*, and P. J. EDMUNDS, B.A., *Queen's College, Oxford*\*

1. **T**HE discharge of electricity through gases in those cases where the electric field is not uniform is attended by phenomena which are absent in the case of the uniform fields produced between plane electrodes. The case in which the electrodes are concentric cylinders has been chosen by various investigators as showing these phenomena

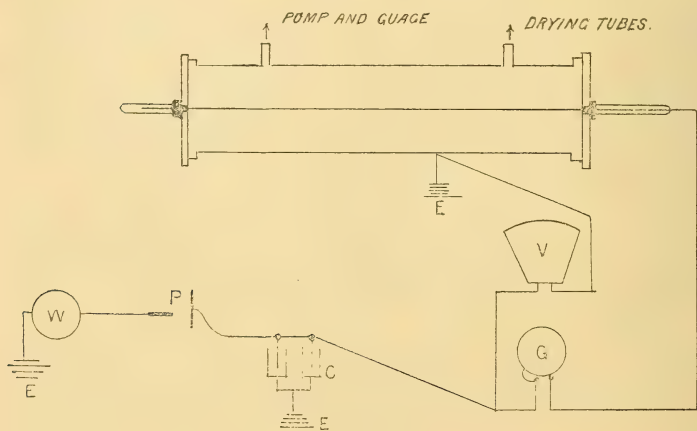
\* Communicated by the Authors.

in a marked degree and also lending itself to mathematical treatment. Some preliminary investigations were made by Baille and Gaugain, but the latest and most complete sets of measurements are those of Watson\*, who investigated discharges through air at pressures varying from one atmosphere to half an atmosphere and with wires between 12·8 and ·7 millimetres diameter.

It was found† that an explanation of Watson's results could be obtained on the hypothesis that the ionization was due to collision, as had previously been found for discharges between parallel plates at low pressures. The present investigation was undertaken to test the theory over a range of pressures of air from one millimetre to 760 mm. with wires of various diameters.

2. For this purpose two cylinders of brass were used; a large one, internal diameter 14·9 cm. and effective length 66 cm., and a smaller one, internal diameter 3·96 cm. and length 44 cm. These cylinders were fitted with outlet and inlet tubes in the sides for exhausting and admitting air, and the ends were closed by thick glass disks through the centres of which wires of various diameters could be inserted and fixed. The free ends of the wires were enclosed in sealed glass tubes, and the ends connected to the instruments were shielded for some six inches by glass tubes and the

Fig. 1.



rest by rubber tubing. The arrangement of the apparatus is shown in the accompanying diagram, figure 1.

\* E. A. Watson, 'The Electrician,' Feb. 11th, 1910.

† See 'Electrician,' June 6th, 1913.

The source of supply was a Wimshurst machine W, driven by a small motor, and the insulated system was charged by the discharge from a point, P, to a plane. The rate of supply could be regulated by altering the distance between the point and the plane.

The potential was determined by an electrostatic voltmeter, V, connected to the insulated system, and the cylinder, which was permanently connected to earth.

A table galvanometer, G, of the moving-coil type, was used to measure the current from the wire to the cylinder. It was sufficiently sensitive to detect a current of about  $2 \times 10^{-9}$  ampere per centimetre length of the wire. The galvanometer was insulated from the table by blocks of paraffin wax; one terminal of the coil was connected to the case and to the voltmeter, the other directly to the wire inside the cylinder. Under these conditions the insulation was quite good and the system would remain charged for a considerable period. In many of the experiments leyden-jars, C, were connected to the insulated system to nullify irregularities in the supply.

It was, however, found that, in certain cases, more steady currents could be obtained without the extra capacity. This was particularly the case when working with low pressures and the wire negatively charged. In these cases there was a tendency to a "spark discharge" as distinct from the "glow discharge." The effect of the spark discharge was to discharge the system to a potential considerably lower than that at which a discharge commenced, thus rendering the discharge discontinuous. By cutting out the leyden-jars the capacity of the system was reduced to a very small quantity, and there was not enough electricity immediately available to supply a current sufficiently large to make a large change in the distribution of electric force. The discharge then became sensibly continuous.

3. The potential necessary to produce the spark was found to be the same as that sufficient to maintain the smallest current detectable with the instruments, and so either was taken as the sparking potential. In all cases except where special mention is made the air used was dried by drawing it slowly through three drying-tubes of about two feet each in length, the first filled with calcium chloride and the other two tightly packed with phosphorus pentoxide. Just before entering the cylinders the air was drawn through a plate of unglazed porcelain to free it from dust.

Irregularities frequently occurred in the negative discharges which have been attributed to dust settling on the



wire. In these cases the discharge could be seen to take place from one point of the wire and the sparking potential may then be considerably reduced. In order to get consistent results with the glow discharges it is necessary that the glow should cover the wire uniformly.

The general appearance of the discharges was closely similar to that described by Watson. All the inner cylinders, except the largest which was of brass rod, were of copper wire and they were cleaned and polished with metal polish and rouge before use. Wires of five different sizes were used, the largest being .476 cm. in diameter and the smallest .006 cm. in diameter.

4. On the hypothesis that the sparking potential is determined by ionization by collision a relation can be found between the force  $X_1$  at the surface of the wire,  $a_1$  the radius of the wire and  $p_1$  the pressure of the gas\*.

In general, let  $V$  be the potential that produces sparking through a gas at pressure  $p$  between any two conductors  $A$  and  $B$ . It may be shown that  $V$  is also the sparking potential for two conductors  $A'$  and  $B'$ , obtained from  $A$  and  $B$  by reducing the linear dimensions in the proportion  $1/k$ , when the pressure  $p'$  is  $kp$ .

Let  $P$  and  $Q$  be two points on a line of force between  $A$  and  $B$ ,  $P'$  and  $Q'$  the corresponding points between  $A'$  and  $B'$ . The number of ions generated by a negative ion in going from  $P$  to  $Q$  is  $\alpha ds$  and from  $P'$  and  $Q'$  is  $\alpha' ds'$ .

$$\text{But} \quad \alpha' = p' f' \left( \frac{X'}{p'} \right) = k p f \left( \frac{X}{p} \right)$$

$$\text{and} \quad ds' = \frac{1}{k} ds;$$

$$\text{therefore} \quad \alpha' ds' = \alpha ds,$$

similarly for positive ions

$$\beta ds = \beta' ds'.$$

Hence the same effects are produced in corresponding paths in the two cases, so that if the potential  $V$  produces a spark in the first case, it will also produce a spark in the second case. Hence the sparking potential  $V$  for a pair of cylinders of radii  $a$  and  $A$  when the pressure is  $p$  is the same as that for a pair of cylinders of radii  $ka$  and  $kA$  when the pressure is  $p/k$ . With the first pair the force  $X_1$  at the

\* Townsend, 'Electrician,' June 6th, 1913.

surface of the inner cylinder is  $V/a \log A/a$ ; and with the second pair the force is  $V/ka \log A/a$ .

Hence  $aX_1$  is constant when  $ap$  is constant for pairs of cylinders which are geometrically similar. Now Gaugain\* found that the force at the surface of a given wire, necessary to produce a discharge, was independent of the radius of the outer cylinder. In all his experiments, however, the radius of the outer cylinder was large compared with that of the inner, the pressure being atmospheric, and Baille† found later that if the difference between the radii was small enough the force at the inner surface was affected by the radius of the outer cylinder, the force increasing when this radius was decreased beyond a certain point.

The ionization due to collision outside the cylindrical surface at which  $X/p=40$  is too small to affect materially the sparking potential, and the condition that the force  $X_1$  should be independent of the radius of the outer cylinder is that  $X_0/p$  should be less than 40,  $X_0$  being the force at the outer cylinder.

5. In the results used in the following discussion  $X_0/p$  was always less than 40. Hence the theory gives the simple result that  $aX_1$  should be the same for all wires for the same value of  $ap$ . To test this a curve, giving the relation between the sparking potential and the pressure, was drawn for each wire; these curves were found to be quite regular and that obtained with a wire 2.38 millimetres radius in a cylinder 7.45 cm. radius is shown as an example (fig. 2, p. 799). It will be noticed that the curves for negative and positive wires cross at about four millimetres pressure.

Between the pressures  $p=3$  and  $p=7$  the negative sparking potential changes from 800 volts to 1700 volts. Between these pressures the sparking potential was very irregular.

Similar remarks apply to some of the values obtained from the cylinders II., where the radii were .063 and 1.98 cm. respectively. For this reason some of the figures in the following tables are enclosed in square brackets and are not considered in finding the mean values. This irregularity did not occur with the smaller wires.

The following tables give the values of  $aX_1$  corresponding to a series of values of  $ap$ . The numbers in the different columns are obtained from the sparking potential curves for cylinders of different radii.

\* J. M. Gaugain, *Ann. de Chim. et de Phys.* (4) viii. (1866).

† Baille, *Ann. de Chim. et de Phys.* (5) xxv. (1882).

$aX_1$  in Volts. Wire positively charged.

$ap.$	I. $A=7.45$ $a=.238$	II. $A=1.98$ $a=.063$	III. $A=7.45$ $a=.046$	IV. $A=1.98$ $a=.046$	V. $A=1.98$ $a=.0115$	VI. $A=7.45$ $a=.0115$	VII. $A=1.98$ $a=.003$	VIII. $A=7.45$ $a=.003$	Mean.
.05	...	...	...	...	...	145	...	147	146
.1	...	...	...	...	...	159	...	163	161
.25	...	206	196	189	...	200	216	201	201
.5	...	259	244	266	244	253	270	256	256
.7	282	288	277	295	280	293	309	301	291
1.0	339	325	316	346	329	347	370	365	342
1.5	407	402	395	403	405	432	463	461	421
2	429	494	472	474	457	495	540	544	466
3	565	583	590	606	611	647	...	...	600
4	675	717	717	731	727	774	...	...	723
6	880	930	914	930	946	...	...	...	920
8	1080	1120	1110	1130	1140	...	...	...	1120
10	1250	1320	1310	1330	...	...	...	...	1290
12	1420	1500	...	...	...	...	...	...	1460
14	1580	1680	...	...	...	...	...	...	1630
16	1750	1860	...	...	...	...	...	...	1790
18	1920	2010	...	...	...	...	...	...	1960
20	2080	...	...	...	...	...	...	...	2080

A radius of outer cylinder.

a radius of inner cylinder.

 $aX_1$  in volts. Wire negatively charged.

$ap.$	I. $A=7.45$ $a=.238$	II. $A=1.98$ $a=.063$	III. $A=7.45$ $a=.046$	IV. $A=1.98$ $a=.046$	V. $A=1.98$ $a=.0115$	VI. $A=7.45$ $a=.0115$	VII. $A=1.98$ $a=.003$	VIII. $A=7.45$ $a=.003$	Mean.
.05	...	...	...	...	...	100	...	115	107
.1	...	131	...	...	...	131	...	141	134
.25	...	145	175	159	138	177	185	193	167
.5	...	189	267	189	244	239	262	256	234
.7	...	224	321	266	294	293	309	301	287
1.0	[339]	[253]	382	348	350	363	370	365	366
1.5	[466]	[311]	456	465	442	455	463	461	457
2	552	[378]	560	554	524	542	555	544	547
3	664	697	707	700	672	686	...	...	688
4	780	834	855	848	808	830	...	...	835
6	998	1070	1040	1070	1060	...	...	...	1050
8	1200	1280	1280	1290	1290	...	...	...	1270
10	1400	1480	1480	1470	...	...	...	...	1460
12	1590	1670	...	...	...	...	...	...	1630
14	1760	1860	...	...	...	...	...	...	1810
16	1950	2040	...	...	...	...	...	...	1990
18	2110	2240	...	...	...	...	...	...	2170
20	2240	...	...	...	...	...	...	...	2240

A radius of outer cylinder

a radius of inner cylinder.

It will be seen that nearly all the results are within five per cent. of the mean in each case. It is remarkable that the results are in such good agreement considering the variation which must have been produced by the chemical action of the discharge on the gas. From the mean results curves have been drawn showing the relation between  $\alpha X_1$  and  $ap$  over the range  $ap = .05$  to  $ap = 20$  (figs. 3 & 4).

Watson's results may be represented in a similar manner. In his experiments eight different sized wires were used, and it is seen from figure 5 that the points lie very well on a curve, which covers the range from  $ap = 20$  to  $ap = 350$ .

6. In the present investigation there was observed in general a marked difference between the sparking potentials when the wire was charged positively and when the wire was charged negatively. For this reason separate curves are given for the values of  $ap$  less than 20. At the smaller values of  $ap$  the sparking potential was found to be lower when the wire was negative than when it was positive; this is in accordance with Meservey's\* results on the discharges from wires in gases at low pressures. But for the larger values of  $ap$  investigated, that is to say with  $ap$  about 5 to 20, a lower potential was required to produce a positive discharge. This is contrary to the generally accepted view; also, Watson observed no material difference between the two cases; however, most of his measurements were made with much larger values of  $ap$ .

The theory indicates that there should be some similar phenomenon in the case of the discharge of electricity from blunt points. A large number of measurements have been made by Zeleny† of the sparking potentials of points to planes, the exact shape of the points being defined, as, for example, cylindrical wires with ends rounded approximately to hemispheres. His measurements were nearly all made at atmospheric pressure. With the discharges from the rounded ends of fine wires the sparking potential with the wire negatively charged was lower than with the point positively charged. However, as the size of the wire was increased, this difference decreased regularly, and with a wire .05 cm. in diameter the sparking potentials were the same for the two cases. But Zeleny gives no results for negative discharges from points larger than .05 cm. diameter.

7. As this required further investigation the discharges from the ends of wires of diameters .05, .1, and .15 centimetre were investigated.

\* A. B. Meservey, *Phil. Mag.* [6] xxi. p. 479.

† Zeleny, *Phys. Rev.* xxv. p. 305 (1907).



The points were made of platinum or silver wire with ends approximately hemispherical, and the planes to which the discharges took place were platinized brass and were fixed at right angles to the axis of the wire. The points and planes were contained under bell-jars fitted with tubes for adjusting the pressure of the air, and measurements of the sparking potentials were made as with the cylinders.

The results showed the same characteristics as those obtained with the cylinders, as may be seen from the following figures:—

	Pressure in mm.	Positive sparking potential in volts.	Negative sparking potential in volts.
Diameter of wire 15 cm. ....	555	6200	7000
Distance from plane 1.5 cm. ...	397	5080	5500
	220	3450	3800
	103	2200	2450
	35	1320	1280
	13	975	825
Diameter of wire 10 cm. ....	763	6400	6800
Distance from plane 10 cm. ...	213	2950	3130
	81	1700	1700
Diameter of wire 0.5 cm. ....	760	5300	5300
Distance from plane 1.5 cm. ...	265	2900	2700

8. It is interesting to see whether this result can be explained on the hypothesis that the effect is due to ionization by collision.

The relation \* which must hold between the values of  $\alpha$  and  $\beta$  along a radius  $r$  between two cylinders, radii  $a$  and  $A$ , before a continuous discharge can take place is

$$I = \int_a^A \alpha e^{-\int_a^r (\alpha - \beta) dr} dr,$$

when the inner cylinder is negatively charged.

The corresponding condition for the case in which the inner cylinder is positively charged is obtained by interchanging  $\alpha$  and  $\beta$  in the above integral, and it does not follow that a system of values of  $\alpha$  and  $\beta$  which satisfies the first also satisfies the second. Hence the system of forces required for a positive discharge is in general different from the system required to maintain a negative discharge.

\* 'Ionization of Gases by Collision,' p. 66.

The effect of concentrating the force near an electrode may be seen by considering the case in which the system of forces between two conductors is slightly less than that which is required to produce a discharge. If the integral

$$\int_0^l \alpha e^{-\int_0^s (\alpha - \beta) ds} ds$$

along the path of the discharge is slightly less than unity, it may be brought up to the required value by increasing the force for a short distance  $ds$  either at the positive or at the negative electrode.

If  $\alpha$  and  $\beta$  be increased to  $\alpha + \delta\alpha_1$  and  $\beta + \delta\beta_1$  from  $s=0$  to  $s=\delta s$  then the increase in the integral is  $\delta\beta_1\delta s$ . If  $\alpha$  and  $\beta$  be increased to  $\alpha + \delta\alpha_2$ , and  $\beta + \delta\beta_2$  from  $s=l-\delta s$  to  $s=l$  the increase in the integral is

$$\delta s \delta\alpha_2 e^{-\int_0^l (\alpha - \beta) ds}.$$

Hence, it is more advantageous to increase the force at the negative electrode than at the positive if

$$\frac{d\beta_1}{dX} \text{ exceeds } \frac{d\alpha_2}{dX} e^{-\int_0^l (\alpha - \beta) ds}.$$

For the case of a uniform field the condition for sparking is

$$\beta = \alpha e^{-(\alpha - \beta)l}.$$

Hence, if the uniform force is not great enough to produce a discharge, it is more advantageous to increase the force at the negative electrode than at the positive electrode if

$$\frac{1}{\beta} \frac{d\beta}{dX} > \frac{1}{\alpha} \frac{d\alpha}{dX}.$$

The determinations of  $\alpha/p$  and  $\beta/p$  that have been made for the larger values of  $X/p$ , from  $X/p=150$  to  $500$ , show that over this range the quantity  $\frac{1}{\beta} \frac{d\beta}{dX}$  is greater than  $\frac{1}{\alpha} \frac{d\alpha}{dX}$  and the discharges are generally obtained more easily when the force is concentrated at the negative electrode. The sparking potentials are comparatively small in these cases, but as  $X/p$  diminishes the sparking potentials increase and the effect of concentrating the force at the negative electrode may be quite different.

It would, however, be impossible to find from theoretical

considerations the difference between the sparking potentials for positive and negative discharges when the potentials are large, as the values of  $\beta/p$  corresponding to the smaller values of  $X/p$ , from  $X/p=40$  to 150, have not yet been determined accurately.

The fact that the positive discharges are produced by smaller potentials than the negative discharges in these cases is not contrary to the theory, since it is quite possible that  $\frac{1}{\beta} \frac{d\beta}{dX}$  may become small in comparison with  $\frac{1}{\alpha} \frac{d\alpha}{dX}$  when  $X/p$  is between the limits 40 to 150.

The above investigations apply to cases in which the ions are generated in a space near the inner cylinder, and the force  $X_0$  at the surface of the outer cylinder is less than  $40 \times p$ .

9. The effect on the sparking potential when the outer cylinder is so small that  $\frac{X_0}{p}$  is greater than 40 is shown by a measurement of the sparking potential obtained with a pressure of 1.35 millimetre between cylinders of radii .063 cm. and 1.98 cm. When the wire was positively charged the sparking potential was found to be 640 volts. This gives  $\frac{X_0}{p}=69$ . Hence it is to be expected that the value of  $\alpha X_1$  should be higher than that obtained in other cases where  $\frac{X_0}{p}$  is less than 40; for the outer cylinder cuts off part of the region where the force is large enough to produce a considerable amount of ionization. The value of  $\alpha X_1$  obtained from the above result is 186, which is, in fact, considerably higher than the value 150 taken from the curve for the same value, 0.85, of  $a/p$ . On the other hand, the negative sparking potential for the same cylinders and air-pressure was found to be 420 volts, giving  $\alpha X_1=122$ , which agrees with the value 118 taken from the curve. This is quite consistent since the value of  $X_0/p$  is only 45.

10. Some observations were also made of the relation of the rise in potential to the current and also of the effect of moisture. It was found impossible to work with very damp air without completely reconstructing the apparatus as the moisture settled on the surfaces of the insulators. However, some experiments were made with air taken from the room and freed from dust without being dried. This amount of moisture had no appreciable effect on the sparking potentials, but the increase of potential required to maintain

Fig. 2.  
Sparking Potentials.  
Radius of inner cylinder .238 cm.  
" outer cylinder 7.45 cm.

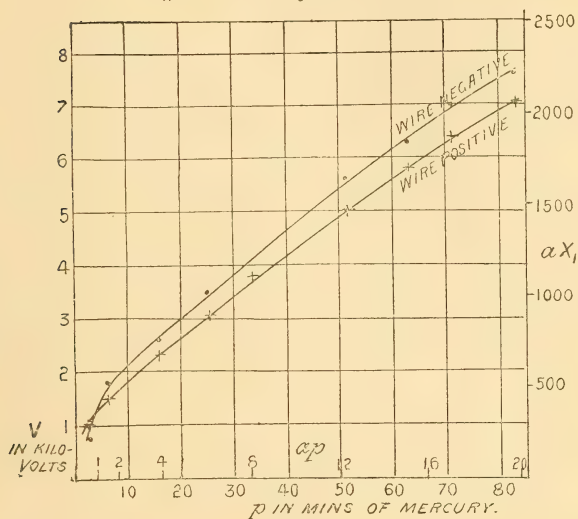


Fig. 3.

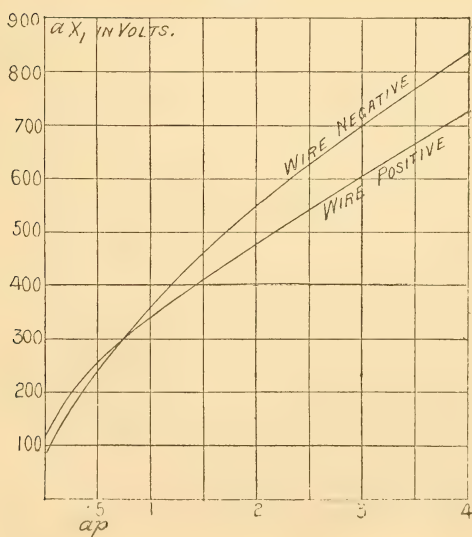




Fig. 4.

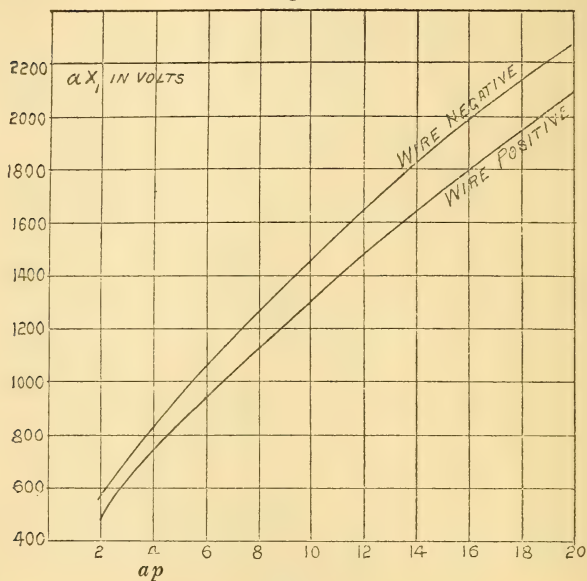
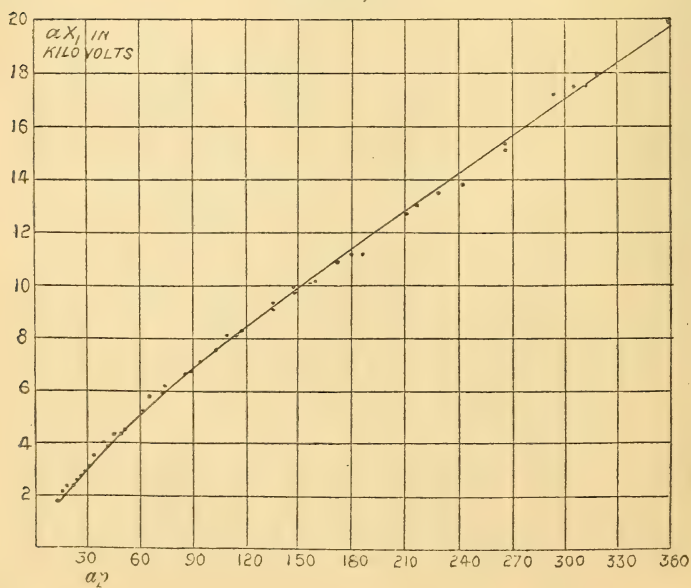


Fig. 5.

Results taken from paper by E. A. Watson, 'Electrician,'  
Feb. 11th, 1910.



a given negative discharge depended on the dryness of the air. The theory shows that the potential  $v$  required to maintain a small current  $I$  is given by the formula

$$v(v - V) = \frac{IA^2 \log A/a}{2k},$$

$k$  being the velocity of the ions under unit electric force and  $V$  the sparking potential. The potentials  $v$  required to maintain small currents were quite consistent with this expression, but no very accurate determinations of  $k$  have yet been deduced from the observations.

It was found that  $dI/dv$  was smaller for positive discharges than for negative discharges. Also when the air was damp,  $dI/dv$  for negative discharges diminished, showing that the negative ions, in the space in which  $a/p$  is small, are affected by the moisture. But in the space near the inner cylinder where  $X/p$  is large the negative ions are not affected by the moisture since the sparking potentials are the same for moist and dry gases.

XC. *The Spectroscopy of the Electric Brush Discharge in Weak Acids and Solutions.* By HAROLD SMITH, M.Sc. (1851 Exhibitioner)\*.

[Plate XI.]

*Introduction.*

THE changes which occur in the spectra of the electric brush discharge in solutions under varying electrical conditions have already been investigated in a previous paper †. In the experiments there considered the brush was produced by means of a large induction-coil, the primary of which was fed with alternating current. The secondary terminals were connected to two electrodes immersed in a small cell containing water or some dilute solution. One of these electrodes was an inch square of platinum foil; the other was a platinum wire fused into a glass tube, with the protruding end of the wire filed till it was flush with the glass. A luminous brush occurred at the end thus exposed. A condenser was arranged in parallel with the cell and an adjustable spark-gap in series with it when a condensed brush was required. Striking variations in the spectra were found according to the nature of the solution, its concentration, and the type of discharge used. Other variations occur when

\* Communicated by Prof. Sir J. J. Thomson, O.M., F.R.S.

† Phil. Mag. [6] vol. xxv. p. 461 (1913).

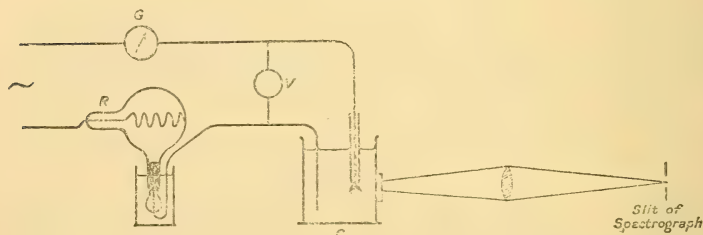
the discharge is made to pass through a very fine capillary in the solution, the spectra of the capillary discharge having quite distinct features from those of the brush spectra.

These variations are discussed in the paper referred to, but the observations were confined to the visible region ( $\lambda=6700 \text{ \AA.}$  to  $\lambda=4200 \text{ \AA.}$ ), and the brush in all cases was alternating. The present research was undertaken to extend the observations into the ultra-violet region and to investigate the differences which may occur between the positive and the negative brush. A large number of solutions was examined, but observations were confined to the uncondensed brush only.

#### *Apparatus.*

In fig. 1 is given a diagram of the apparatus used in these experiments. The brush was produced in the cell, C, which contained a litre of the solution under examination, and was provided with a quartz window affixed with sealing-wax.

Fig. 1.



An image of the brush was focussed by means of a simple quartz condensing lens (3 in. focus) onto the slit of a small quartz spectrograph. The potential difference between the electrodes was measured by means of an electrostatic voltmeter, V, and the current through the brush by means of a galvanometer, G. The coil and outside case of the galvanometer were connected together and earthed in order to avoid electrostatic effects. A Lodge valve, R, was used to rectify the current, a positive or negative brush being produced simply by reversing the valve. The anode of the valve was kept immersed in water, as it otherwise became very hot during a series of exposures and was very liable to crack. Instead of an induction-coil, a large transformer immersed in oil was used. The spectrograph employed gave a very small dispersion in the visible part of the spectrum; the total length of spectrum from  $\lambda 6563$  to  $\lambda 2400$  was a little less than 4.5 cms.

Platinum wire about .5 mm. in diameter was used in the construction of the points, one point lasting usually for two exposures. Copper wire of about the same diameter was used in a few trial experiments, but was not satisfactory. For the negative brush it acted as well as platinum, but the positive brush caused the glass to crumble rapidly away.

*Features of the Brush.*

The general features of the brush when it is not unipolar have already been described \*. Differences occur according to the sign of the brush which call for further description. In distilled water each brush consists of a bundle of very fine filaments (fig. 2). Unless the point has been filed

Fig. 2.



Brush (+ or -) in distilled water.

[Figs. 2 to 5 represent brush enlarged about twice.]

very carefully the brush in either case may split in two, each brush springing from a point on the edge of the platinum wire where it touches the glass. The positive brush is shorter than the negative and emits a brilliant rose-red light. The greatest length attained by the negative brush is about 5 mm. It emits a pale blue light, almost white in its intensity. A slight rise in conductivity of the water causes the colour to change to red, though it never attains to the bright rose-red of the positive brush. As the conductivity rises (the increase due to the rise in temperature produced by the action of the brush is sufficient), the filaments of the positive brush thicken, diminish considerably in number, and emit a somewhat feebler light. Under the same circumstance the negative brush shrinks, grows fainter, and at length emits a feeble blue light with yellow close to the point. If the current in the transformer primary is kept constant, these changes are accompanied by an increase of

\* Smith, *l.c.*



current through the brush and a large decrease of potential difference between the electrodes, the decrease being greatest for the negative brush. When once the water has become warm no amount of variation of the current in the transformer primary will restore the brush characteristic of cold distilled water.

The positive brush in cold distilled water is more silent than the negative brush, though both make a hissing noise. A steady stream of fine bubbles is ejected from the positive point. The bubbles from the negative point are shot out in a cloud from the brush and the water is kept in considerable agitation.

When the conductivity of the water is increased by the addition of a little acid or some salt, the negative brush changes into a short luminous tongue about 1 to 2 mm. long.

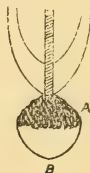
Fig. 3.



Negative Brush in Solutions.

It is unsteady, and does not appear to be separated into filaments (fig. 3). In acids it emits a yellow light due to some sodium salt present in solution as an impurity. In salt solutions it emits a light according to the salt dissolved—red for lithium salts, green for copper, blue for zinc, etc. The positive brush is a little longer than the negative and much

Fig. 4.



Positive Brush in Solutions. Discharge (A) in constant agitation. Bubbles are emitted from apex B.

broader, about from 2 to 3 mm. across. It consists of a pale blue discharge spread over what appears to be the top of a bubble, so that it has an umbrella-like shape (fig. 4).

Viewed through a low-power microscope it appears in constant agitation. There is a bright luminous spot close to the point. The positive brush in the strongest solutions is coloured slightly according to the salt in solution.

The change from the type of brush characteristic of distilled water to that characteristic of a solution occurs suddenly at a certain concentration. The same concentration is not required for each brush; a slightly stronger solution generally being required for the positive brush than for the negative. In sodium, magnesium, and zinc sulphate solutions the reverse was the case. With zinc sulphate, especially, the negative brush did not change to the solution type till a concentration of .1 per cent. was reached, while the positive brush acquired the solution characteristic at a concentration of .005 per cent., the usual concentration at which the change occurs.

In solutions, the bubbles are emitted from each point much less vigorously than in distilled water. The bubbles are also much fewer in number and a good deal larger. In the case of the negative brush, the bubbles seem to be emitted from all parts of the brush. In the case of the positive brush, the bubbles are emitted only from the bottom of the stationary bubble (fig. 4). The sound given out by the positive brush is harsh, much harsher than that given out by the negative.

In either brush, if the current is strong, the emission of bubbles from the point may cease, while a large bubble forms under the point and grows slowly, portions detaching from it at intervals of several seconds. This bubble may last for some time; generally, however, it breaks away after a few seconds, and is succeeded by an emission of small bubbles which lasts for a similar time, after which the large bubble forms once more. In dilute acids, especially of sulphuric acid, this "bubble formation" occurs much more readily at the positive point than at the negative, and attains its greatest size (4 or 5 mm. across) at the former. This statement holds more or less for salt solutions also. In alkaline solutions (LiOH, NaOH, KOH) the bubble occurred only at the negative point. There seems to be a concentration at which the bubble forms most readily. Inversion of the point prevents a large bubble from forming, but a smaller bubble continues to form at the negative point. This type of "bubble formation" is quite distinct from that described above and represented in fig. 4; a drawing of it is shown in fig. 5.

This bubble seems to have little effect upon the spectrum in general. In salt solutions when the brush is negative, there is a brightening of the spectrum as a whole, especially of the metal lines of the salt in solution and of the continuous background. Its formation is accompanied by a rise in potential.

In sulphuric acid, the bubble soon after its formation becomes suffused with a beautiful violet colour, which commences near the top and then spreads downwards till the whole bubble is filled with the glow. This condition lasts for a few seconds, when the bubble breaks up and the whole process is gone through once more. Bubbles, similarly coloured, occur in solutions of sulphates, hydrogen sulphide, and sulphur dioxide. The intensity of the light emitted depends upon the concentration of solution. In phosphoric acid a luminous green bubble forms in the same manner. In neither hydrochloric, nitric, molybdic, nor chromic acid solution is the bubble coloured.

Fig. 5.



Bubble formation. In addition to discharge over top of bubble, in Sulphuric Acid the whole bubble glows with luminous violet colour.

The diagrams fig. 2 to fig. 5 represent different types of brush discharge. The separation of the bubble from the point (fig. 5) is commented on in the previous paper. This separation is best shown in the negative brush in sulphuric acid.

#### *Electrical Conditions, &c.*

The potential difference measured by the voltmeter gives a mean value for what is actually a very variable quantity. If the brush be examined in a mirror rotated quickly by hand, it will be seen drawn out into luminous bands separated by dark intervals during which no current is passing. Both the negative and positive brush in distilled water appear as continuous bands which are patchy and crossed with fine lines. The negative brush in solutions appears as narrow

bands of light, more or less patchy, the end and beginning of each band being generally broken up into two or three dots separated by short dark spaces. The positive brush in solutions shows bands broken up throughout their whole length into dots separated by short dark spaces. In magnesium sulphate and zinc sulphate solutions, the negative brush was harsher in sound than in other solutions, and when examined in the rotating mirror, it appeared as bands broken up into a series of dots in the same manner as the positive brush.

As the plate electrode may be moved close up to the brush without any perceptible alteration in the readings of either the voltmeter or galvanometer, the potential difference measured must be very nearly equal to the potential drop through the brush, and may thus be considered as the potential necessary to produce the brush. The minimum potential required, as thus measured, is found to vary according to the sign of the brush and concentration of solution. Some measurements are given in Table I.

TABLE I.

	Minimum Potential in volts.		Conductivity in $\frac{1}{1000}$ mho.	
	+	-	+	-
Distilled water .....	2700	2200	·0013	·0006
NaOH ·001 p. c. ....	1825	1250	·0023	·0024
„ ·005 „ .....	560	300	·041	·052
„ ·01 „ .....	300	200	·052	·106

It will be seen that to produce a positive brush a larger potential is always required than to produce a negative brush, and that the necessary potential decreases with strength of solution. The minimum current, however, varies from 1 or 2 milliamps. for distilled water to about 30 milliamps. for the stronger solutions, *e. g.* 1 per cent. NaOH. The conductivity of distilled water is greater with a positive brush than with a negative. This becomes reversed in solutions.

### *Evolution of Gas.*

Beyond what has already been said concerning the evolution of gas in the brush, there remains a further point which requires mentioning as it may cast a little light on the mechanism of the brush. In an experiment on the decomposition of water, Wollaston used as electrodes two platinum



wires fused into glass tubes with the protruding ends filed flush with the glass. When these electrodes were connected to the terminals of an electric machine, an electrolytic mixture of hydrogen and oxygen was evolved at each pole in equal quantities. Faraday repeated the experiment \*, and found that if a nail was substituted for one electrode no gas was evolved at the nail, while the evolution of gas at the unaltered electrode was the same as before. A spark-gap placed in series with the cell caused a larger evolution of gas for the same number of turns of the machine, the longer the spark-gap the greater being the evolution of gas. In a solution of sodium sulphate, however, even with powerful sparks, he obtained very little gas. In Table II. I give some results obtained in the case of the brush. The gas evolved in all cases was explosive.

TABLE II.

Liquid.	Sign of Brush.	Current in milliamps.	Potential in volts.	Vol. of gas liberated per min. (A). (N. T. P.)	Vol. of gas calculated (B). (N. T. P.)	Ratio A/B.
H <sub>2</sub> O .....	+	11.9	2500	.63 c. c.	.041 c. c.	15.3
„ .....	-	5.7	4250	.55 „	.039 „	14.1
K <sub>2</sub> CO <sub>3</sub> } .65 p. c. }	+	32.3	700	1.55 „	.112 „	13.8
	-	33.9	300	.29 „	.236 „	1.23

In distilled water fifteen times as much gas is evolved as can be accounted for by electrochemical decomposition. When the cell forms part of a condenser and spark-gap circuit, the evolution of gas is considerable and out of all proportion to the quantity which should be evolved by the action of the current.

In solutions, with the uncondensed brush, the evolution of gas is much more considerable at the positive point than at the negative, the evolution at the negative being little more than the calculated amount. Taking this into account with the harsher noise of the positive brush and its intermittent character as shown in the rotating mirror, it would seem that the positive brush consists of a series of small sparks, while the negative brush bears a closer resemblance to an arc. Some of the spectra occurring at the negative brush are either characteristic of an arc or of a type intermediate between the arc and spark.

\* Faraday's Exp. Res. vol. i. §§ 327-331.

*Method of Work.*

Spectrograms of the positive and the negative brush were taken alternately, exposures of a quarter of an hour being given to each. By varying the current in the transformer primary, the current through the brush was kept as nearly constant as possible during the exposure, and for each couple of spectrograms the same current was used. Three readings of current and potential difference were taken during each exposure. Very careful use must be made of these readings to interpret the spectrograms, as they do not take into account the rapid fluctuations which occur both in the positive and negative brush, and which are probably different in each. It will be shown later that changes occur in the spectra which can only be accounted for by supposing changes in the electrical conditions which are not taken into account by the method of measurement adopted. To keep even the mean potential and current constant was quite impossible, though occasionally readings would remain quite steady during the whole exposure.

The liquids examined were distilled water, tap-water, solutions of  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{CrO}_4$ ,  $\text{H}_2\text{MoO}_4$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{NaOH}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaCl}$ ,  $\text{KOH}$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{KBr}$ ,  $\text{LiOH}$ ,  $\text{Li}_2\text{SO}_4$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{MgSO}_4$ ,  $\text{ZnSO}_4$ .

Various concentrations were used (.001 per cent. to .5 per cent. by weight in the case of salts, and from .03 per cent. to 2 per cent. by vol. of concentrated acid in the case of acids), and in a large number the current also was varied. Altogether some 370 photographs were taken.

*Spectrum of the Bubble.*

In discussing the spectra produced I shall first give the results obtained in the case of the "bubble discharge." As was stated above, in the case of dilute sulphuric acid, when a bubble forms underneath the point it becomes suffused with a beautiful violet colour. Though the image thrown on the slit by the quartz lens is not achromatic, it is possible to notice differences in the spectrum near to and remote from the point for a region a little longer than the visible part. The spectrum of the bubble discharge shows not only the usual spectrum produced when there is no bubble, but also a series of bands degraded towards the red and stretching from about  $\text{H}_\beta$  to  $\lambda=3100$ . They are most intense in the region of the H and K lines. While the ordinary brush spectrum is confined quite close to the point,

being in general strongest near the point, these bands are weak close to the point while they are strongest some little distance from the point; they are also very long. These bands are the spectrum of the bubble (figs. 9, 6 *a*, 7 *b*, Pl. XI.).

This spectrum, I find, is identical with the spectrum of the "afterglow" of hydrogen discovered by Prof. Strutt \*. Strutt observed that these bands only appeared when sulphur was present as an impurity, and that their appearance was the most sensitive test for the presence of sulphur in hydrogen. He also observed the spectrum in hydrogen sulphide (afterglow) in the carbon bisulphide flame, and also when sulphur or its compounds was acted on by chemically active nitrogen. When experimenting on the afterglow in hydrogen, he tried unsuccessfully to produce the spectrum in pure sulphur vapour. The same spectrum, I find, had already been observed by Himstedt and von Dechend †. They found that in the glow-discharge in hydrogen, in the region remote from the point there appeared a series of bands degraded towards the red. I have given their values for the wave-lengths of the brightest edges, together with Strutt's for the carbon bisulphide flame and my own for the bubble-discharge spectrum. There can be little doubt that the three spectra are the same.

TABLE III.

Himstedt & von Dechend } (glow-discharge).	404	394	383	374	...	364	...	355
Strutt (carbon bisulphide } flame).	4050	3940	3835	3740	3680	3645	3590	3557
Bubble spectrum .....	4046	3939	3828	3741	3680	3645	3589	3556

The bands at 3680 and 3590 are much fainter than the others. Strutt also gives wave-lengths of the fainter bands extending towards the red and violet. I have not been able to obtain very great accuracy in my own measurements, as the dispersion of the apparatus was so small. The presence of a fainter band a few Ångström units shorter in wave-length than each bright band also made measurements rather confusing. Strutt suggests that the spectrum may be due to sulphur, as it appears when sulphur compounds are acted on by chemically active nitrogen. The spectrum, however, may be as sensitive to a trace of hydrogen in an excess of sulphur, as Strutt as shown the converse to be true. It seems more probable that the spectrum is due to hydrogen

\* Proc. Roy. Soc. vol. lxxxvi. pp. 529-33 (1912).

† *Phys. Zeit.* vol. ix. pp. 852-3 (1908).

sulphide. In all the cases in which it makes its appearance the conditions of excitation are feeble and therefore the temperature probably low. Measurements on the breadths of spectrum lines in Geissler tubes show that the temperature must be approximately room temperature, and that of the glow discharge in the experiment of Himstedt and von Dechend is not likely to be higher. It seems unlikely then that the sulphur should produce a spectrum at room temperature in the part of the discharge only where the conditions of excitation are feeblest, *i. e.* farthest from the point. Sulphur produces its spectra in the vacuum-tube, when it is heated sufficiently to produce a high enough vapour-pressure for the discharge to pass.

The spectrum appears in dilute sulphuric acid, solutions of sulphates, hydrogen sulphide, sulphur dioxide, and in no other solutions where sulphur was not present. It only occurred in those cases where a bubble formed at the point and was the spectrum of the light emitted by the bubble. Phosphoric acid gave a green bubble showing bands in the green which, however, were too faint for spectrographic work. These are the only two acids which were tried which gave coloured bubbles.

*Spectra of the Brush Discharge.*

The spectra which occur in the brush-discharge are those of :—

*Hydrogen* : Series spectrum and secondary spectrum.

*Solute* : Spectrum of the metal of dissolved salt.

*Oxygen* : Series spectrum and elementary line spectrum.

*Water vapour* : Ultra-violet band spectrum.

*Electrode* : Arc spectrum (platinum).

*Impurities* : Nitrogen (positive and negative band spectra), Calcium, Sodium, Silicon (line and ultra-violet band spectrum), and Lead (arc) spectra.

The spectrum characteristic of distilled water differs somewhat in the two discharges. The negative brush, which is blue in the most highly resistant water, shows a continuous background stretching from the red to about  $\lambda 3300$ . It is strongest photographically between  $\lambda 4861$  and  $\lambda 3800$  (fig. 4 *b*, Pl. XI.), and it is to this that the blue colour is due. As the conductivity rises, the brush becomes pinker and the continuous spectrum fades (fig. 4 *c*). The spectrum of the positive brush contains very little continuous background (fig. 4 *a*).



In solutions the spectrum is often free from any continuous background ; on the other hand, the background is occasionally for a few seconds very bright, especially in the case of the negative brush. During the "bubble formation" at the negative point a continuous background is always developed.

### *Hydrogen.*

The hydrogen spectra appear best in distilled water.  $H_{\alpha}$ ,  $H_{\beta}$ ,  $H_{\gamma}$  are very bright, while  $H_{\delta}$  and  $H_{\epsilon}$ , though readily discernible, are much fainter. Relative to the series lines the secondary is much fainter than is the case for the spectrum of dry hydrogen in a Geissler tube. For the same current through the brush, the hydrogen lines are a little weaker at the positive than at the negative point (fig. 4 *a, b*). In this case, the potential is much greater for the negative brush than for the positive. If the potential is the same in each case, the current through the positive brush is much the larger and the hydrogen lines brighter than in the negative brush (fig. 3). The intensity of the series lines falls off more rapidly towards the violet in the case of the negative brush than in the case of the positive.

As the water increases in conductivity the potential falls rapidly, even with a large increase in current, and the hydrogen lines decrease rapidly in intensity. In solutions, the spectrum is generally too weak to show any trace of the secondary spectrum. When each brush has changed over to the solution type, it is found that for the same current through the brush the hydrogen lines are of about equal intensity in each spectrum, although the potential is greater for the positive brush. This is the case no matter whether the solution is acid, alkaline, or contains some neutral salt. In very weak solutions, where one brush retains the form characteristic of the brush in distilled water, then, no matter what the sign of the brush, the hydrogen lines are stronger in it than in the brush which has changed over to the solution type.

In Pl. XI. fig. 7 are given reproductions of three spectra of the negative brush, taken on the same plate and given the same exposure. The brush was produced in distilled water, dilute sulphuric acid, and a solution of caustic potash. The hydrogen lines are of about equal intensity in each. In the two solutions, it will be seen that about the same current and a low potential are required for each ; while in distilled water a much smaller current with a larger potential gave the same intensity of spectrum.

It will be seen from this that the intensity of the spectra is a function both of the current and the potential. Indeed, the hydrogen spectra depend upon the potential to a very much greater extent than do any of the other spectra. As neither the nature of the ions present nor the sign of the brush has much effect upon the spectra, electrolytic action can have little bearing upon their appearance.

*Solute.*

In all salt solutions the spectrum of the metal appears at the negative pole only, when the solution is weak; in the strongest solutions they begin to appear at the positive pole faintly (Pl. XI. fig. 2, *d, e, f*). For constant current, the spectrum of the metal increases in intensity with increasing concentration, but reaches a maximum for the salts of the alkali metals at a strength of solution between .005 per cent. and .01 per cent. For magnesium sulphate the concentration was .02 per cent.; for zinc sulphate .1 per cent. Thereafter, with slight fluctuations, it retains the same intensity for further concentration, diminishing in intensity at length with the rest of the spectrum as the potential begins to fall toward the minimum value (figs. 1 & 2).

An experiment was described in the previous paper which showed that the solution spectrum is produced in strength only in the neighbourhood of an electrode. Two vessels, placed one inside the other, were filled with solution and platinum wires immersed in each as electrodes. The current flowed from one electrode to the other through a very fine capillary in the inner vessel and rendered the capillary luminous. The hydrogen lines were produced brightly, but even in the strongest solutions the metallic solution lines were very weak. When the wire electrode of the inner vessel was made to touch the top of the capillary, its tip became surrounded with a luminous glow which besides giving the hydrogen lines yielded the spectrum of the metal of the salt in solution very brightly.

These phenomena receive a simple explanation from the point of view of electrolysis. In the case of a capillary, the metallic ions merely pass up through the capillary with the current; there is no increase in their concentration, and their spectrum is consequently very weak. In the case of the platinum point electrode, the metallic ions move up to the negative electrode and accumulate there. Consequently a greater quantity of metal is concentrated in the neighbourhood of the brush, and a very bright spectrum is the result. As the concentration of solution increases, the

quantity which arrives at the point increases till the current (so far as it is due to the motion of the cations) is carried entirely by the metallic ions, and none of it by the hydrogen ions. After this, with constant current, no further increase in the quantity of metal can take place at the negative electrode, and the spectrum in consequence is at its maximum brightness. The appearance of the spectrum at the positive point in the strongest solutions is due to the current being insufficient to remove the metallic cations from the neighbourhood of the point.

If an alternating brush (provided the solution is not too weak) be examined in the rotating mirror, several bands, occurring one after the other, will appear coloured, like the negative brush, according to the salt in solution; several bands will then follow, coloured blue like the positive brush. In the stronger solutions all the bands are coloured like the negative brush. If a positive brush be produced at an electrode which has just before been used in producing a negative, it will appear for the first second or two coloured according to the salt in solution. These experiments show that the ions take some little time to accumulate at or be expelled from the point.

The solution spectrum is the only case where electrolysis plays a definite and important part.

#### *Lithium Salts.*

The lines which appear and are due to lithium are :—

Principal Series.	1st Sub-series.	2nd Sub-series.
6708	6104	4972
	4602	4273
	4132	
	3915	
	3795	

The brightest line of the spectrum in the weaker solutions was the red line  $\lambda=6708$ . The lines of the 1st Sub-series,  $\lambda=6104$  and  $\lambda=4602$ , approached it in brightness as the strength of solution increased. Finally, the blue line  $\lambda=4602$  became brighter than the red line nearest the point. The red line was always the longest line in the spectrum. An increase in current produced a similar effect to an increase in concentration, but was not very marked. This variation is most probably connected with the amount of lithium liberated at the point. The line  $\lambda=6708$  is the ultimate ray of lithium persisting longest as the quantity of

metal is gradually diminished. An increase in the quantity of metal diminishes its relative intensity to the rest of the spectrum.

*Sodium Salts.*

The lines which appear and are due to sodium are :—

Principal Series.	1st Sub-series.	2nd Sub-series.
5893	5685	6163
3303	4981	5152
2853	4667	4755
	4492	4544
	4392 ?	

The most brilliant line in the spectrum is the D doublet (unresolved). No variation in relative intensity of the lines has been detected save in one or two instances, where lines of the 1st Sub-series have appeared close to the point, while the D line has been weakest close to the point.

*Potassium Salts.*

The lines which occur and are due to potassium are :—

Principal Series.
4045
3447

The line  $\lambda=4045$  is very strong, while the line  $\lambda=3447$  is very faint. These are the only lines in the spectrum which appear. The following lines, with intensity in brackets, appear at the negative point in all solutions of potassium salts, and in no other solutions. I have been unable to identify them :—

3814 (10)
3798 (5)
3780 (1)

*Copper Nitrate.*

The lines due to copper are :—

2442 (2),	2619 (5),	3247 (10),	3274 (10),
4023 (1),	4063 (3),	4275 (1),	4651 (1),
5106 (2),	5153 (1),	5218 (3).	

The same spectrum appears in each brush when a copper point is used instead of platinum.



816 Mr. H. Smith on the Spectroscopy of the Electric  
Zinc Sulphate.

The lines due to zinc are :—

1st Sub-series.	2nd Sub-series.
$\left\{ \begin{array}{l} 3282 \quad 2802 \quad 2771 \\ 3303 \\ 3346 \end{array} \right.$	$\left\{ \begin{array}{l} 4680 \\ 4722 \\ 4811 \end{array} \right. \left\{ \begin{array}{l} 3072 \\ 3034 \\ [3019] \end{array} \right.$

The arc line 6364 is very weak, while spark lines appear faintly at 2502, 2558, 4912, 4925.

Lines also appear at 424, 465, 450. These occur in the vacuum-tube discharge, in the arc in hydrogen, and in the arc *in vacuo*.

From the intensities of the spectral lines which appear, it will be seen that the spectrum is intermediate between the spark and the arc spectrum.

*Magnesium Sulphate.*

The lines due to magnesium are :—

1st Sub-series.	2nd Sub-series.
$\left\{ \begin{array}{l} 3838 \quad 2852 \\ 3833 \\ 3830 \end{array} \right.$	$\left\{ \begin{array}{l} 5184 \quad 3332 \\ 5173 \\ 5168 \end{array} \right.$

The spark-line at 4481 appears but is rather faint. The lines of the isolated series 5529, 4703, 4352, 4058 are absent. This series is bright in the arc. The spectrum of magnesium, like that of zinc, is intermediate between the spectra of the arc and spark.

A series of bands appears in the ultra-violet between the limits 380 and 368. A band spectrum between these limits occurs which is ascribed by some to magnesium oxide and by others to magnesium. The bands were so crowded on the negative that any closer identification was impossible. The green bands of magnesium oxide were absent.

*Oxygen.*

The elementary line spectrum appears in the brush under certain conditions. In distilled water it appears in the spectrum of each brush, but very faintly in comparison with the hydrogen lines. A slight increase in conductivity causes the spectrum to disappear from the negative brush, while it is strengthened in the positive. As the brush passes over to the solution type, the oxygen lines are further strengthened

in the positive brush, while the hydrogen lines are considerably weakened. As the concentration increases, the lines remain of the same intensity, with slight fluctuations, provided the current is kept constant. The behaviour of the oxygen lines in the positive brush is the same for all solutions.

In acid solutions only the faintest traces of the lines could be detected in the negative brush, and were generally very short and close to the point. Generally the spectrum was entirely absent. In solutions of magnesium sulphate and zinc sulphate, very faint traces were discovered at concentrations less than .005 per cent, but above this none of the lines were discernible. Faint traces of the spectrum occur in tap-water.

In solutions of hydrogen peroxide and of the salts of the alkali metals, the behaviour is quite different. Hydrogen peroxide, however, is not an independent example, as it was very considerably contaminated with sodium. In weak solutions of these salts the spectrum disappeared from the negative brush but reappeared with further concentration. The lines at first were short and faint, being confined close to the point. With further concentration, the current remaining constant, they grew in intensity and length till they were brighter than the hydrogen lines and much brighter than the corresponding spectrum in the positive brush. With further concentration, the spectrum remained approximately of the same intensity for the same current. The concentration at which the oxygen lines reach their maximum intensity lies between .005 per cent. and .01 per cent. It will be seen that the behaviour of the oxygen spectrum in this respect is exactly similar to the behaviour of the metallic lines of the solute (see above). Indeed, the connexion between the spectra is very evident on all the negatives. The connexion, however, is not absolutely rigid, though it is quite definite. After the maximum has been reached for both spectra, one may show a slight increase in intensity in a subsequent spectrogram, while the other shows a slight decrease, and *vice versa*.

In all cases the oxygen lines are brightest close to the point in the negative brush. In this respect they are different from the positive spectrum. Here the lines are long and of unvarying intensity throughout their length, being longer than the hydrogen lines, which in some cases are brighter than they are and in all cases are brightest close to the point. In a few spectra of the positive brush, the oxygen lines stop short a small distance from the point.

In very dilute solutions the line  $\lambda=4368$  of the series spectrum appears distinctly in the negative brush. Wherever the elementary line spectrum appears this line cannot be detected on account of the presence of the lines  $\lambda=4367$  and  $\lambda=4369$  from which it is not separated on account of the low dispersion. Its appearance in the negative brush in very weak solutions where the potential is still high, shows that the absence of the elementary line spectrum is due not to a lack of oxygen but to a change in the electrical conditions. The series spectrum does not appear in the stronger solutions. Its behaviour was shown in the previous paper to be similar to that of the series spectrum of hydrogen.

With the data available it is not possible to settle definitely how the elementary line spectrum arises in the different cases. In air it appears in the spark without self-induction. It is developed in the capillary of a Geissler tube with a condensed discharge when the pressure is sufficiently low. It does not appear in the capillary with the ordinary discharge, but appears together with the negative bands in the neighbourhood of the cathode. That the spectrum should appear in the positive brush is not surprising considering its spark-like character. To see whether the fluctuations in the current were responsible for the spectrum, a positive brush was placed in series with a negative in a solution of sulphuric acid, so that the same current flowed through each brush. The spectrum appeared readily in the positive brush but it was very weak in the negative. A negative brush in caustic potash was then placed in series with the negative brush in dilute sulphuric acid, the two cells being connected with unguarded platinum wire. While the negative brush in caustic potash yielded the oxygen spectrum very brightly, the brush in sulphuric acid showed only traces of the spectrum. Consequently fluctuations in the current seem to have little connexion with the spectrum. A condensed discharge was now sent through the brush in sulphuric acid, the condenser being in parallel with the cell and a spark-gap in series with it. It was found that when the spark-gap was arcing across, the oxygen spectrum was developed quite strongly; when the spark-gap was kept working correctly with an air draft blown across it, the oxygen spectrum could not be detected. On account of the brightness of the continuous spectrum in the latter case, the exposure had to be kept short so that the decrease in intensity in the oxygen spectrum may only be relative. The experiment shows, however, that a change in the electrical conditions will develop the oxygen spectrum in the negative brush in acids.

The negative brush in the salt-solutions of lithium, sodium, and potassium is the same in character as that in dilute acids. The potential required to produce it is smaller than that required to produce the positive brush, the evolution of gas is only slightly more than the calculated amount (see Table II. for .05 per cent. solution  $K_2CO_3$ ), and its appearance in the rotating mirror is a series of unbroken bands. That there is a change in the electrical conditions of the brush is suggested, however, by the behaviour of the nitrogen spectrum (referred to below). There it will be shown that the negative bands of nitrogen behave in a manner almost identical with that of the elementary line spectrum of oxygen. It was shown by Fulcher\* that these bands are produced by more rapidly moving cathode rays than those which produce the positive bands. The connexion between the oxygen spectrum and that of the metal of the dissolved salt (lithium, sodium, or potassium) was pointed out above. This connexion indicates that the spectrum depends in some way on the concentration of the metallic ion at the negative point. In the interval during which no current flows, the metal liberated will form a certain amount of hydrate in solution with the production of hydroxyl ions. As these ions are not swept away from the point immediately the brush occurs, and as they are constantly being renewed, the negative brush will take place in a region containing a large number of hydroxyl ions. These ions, as the source of oxygen, may possibly play an important part in the production of the spectrum.

#### *Water Vapour Bands.*

The ultra-violet bands of water vapour (discovered simultaneously by Huggins † and by Liveing & Dewar ‡) appear strongly in all the spectra and occur equally well in each brush. There is no correspondence between the strength of the bands and the spectra of hydrogen and oxygen. They appear equally well in acids and in alkalies, and so are uninfluenced by an excess of hydrogen or hydroxyl ions. They do not depend, as the hydrogen spectra do, upon a high potential to produce them strongly. If the current in the transformer primary is kept constant, then as the water increases in conductivity the bands increase in intensity as the current through the brush increases and the potential difference between the electrodes falls. The intensity of the bands is not proportional to the current only; a larger

\* Astrophysical Journ. vol. xxxvii. p. 60 (1913).

† Proc. Roy. Soc. vol. xxx. p. 516 (1880).

‡ Proc. Roy. Soc. vol. xxx. p. 580 (1880); vol. xxxiii. p. 274 (1882); vol. clxxix. p. 27 (1888).



current is needed in solutions where the potential is low, to produce them in a definite intensity, than is required in distilled water where the potential is high (Pl. XI. fig. 1a, c).

I have compared these bands with the ultra-violet bands occurring in the cone of a Bunsen flame and with the bands occurring in damp air in a Geissler tube with a quartz window.

#### *Electrode.*

When a platinum wire is used as the electrode in the production of the brush, the arc spectrum appears when the brush is negative. Even with very long exposures, there is no trace of the spectrum in the positive brush (fig. 9 b, c). The lines of platinum are most numerous and strongest in the ultra-violet. Traces of the visible lines, however, sometimes appear, and these are concentrated close to the point. The lines in the ultra-violet, being out of focus on the slit, do not show this. The relative intensity of these lines to the lines in the water-vapour bands is practically constant. There is, however, a certain amount of fluctuation, and in a few cases the platinum spectrum is very weak. In the condensed brush the *spark* spectrum of platinum appears (Pl. XI. fig. 8).

When copper wire is used for the electrode in the production of the brush in distilled water, the lines  $\lambda=3247$  and  $\lambda=3274$  appear faintly in the positive brush and a little more strongly in the negative. In acid solutions the lines are very bright and other lines also appear. This, no doubt, is due to the copper passing into solution.

#### *Nitrogen.*

The bands of the nitrogen spectrum appear in both the negative and positive brush in distilled water. In both cases the positive and negative bands occur. The negative bands are stronger relatively to the positive in the positive brush than in the negative. In the positive brush the edge of the negative band at  $\lambda=3914$  is about equal in intensity with the edge of the positive band  $\lambda=3801$ , and this relation is maintained throughout all solutions, as well as in distilled water.

The presence of the nitrogen spectrum in solutions depends upon the point being more or less cracked. Small cracks do not affect the spectrum in any way except to cause the nitrogen band spectrum to appear. Its presence, however, unless it is very weak, is a serious trouble, as it complicates a spectrum already very crowded with lines. Every care

therefore was taken to keep it out of the spectrum. Consequently there are not a very great number of examples of the bands appearing under varying conditions, and most of these are rather faint. They are, however, sufficiently numerous for one to draw some conclusions with some security. The variation which occurs is a change in relative intensity of the negative bands to the positive in the negative brush. In acid solutions ( $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{S}$ ; other acids do not show the bands in the negative brush) the negative bands disappear from the negative brush. In two cases in nitric acid with a copper point the negative bands appear; in other two cases they are entirely absent even with the positive bands very strong (see fig. 5*b*). In  $\text{LiOH}$ , and  $\text{K}_2\text{SO}_4$  solutions, although the positive bands were weak, the negative band  $\lambda=3914$  appeared distinctly. Better examples occurred in  $\text{Li}_2\text{SO}_4$ ,  $\text{NaOH}$ , and  $\text{NaS}_2\text{SO}_4$  solutions. These photographs revealed the interesting fact that the negative bands increased relatively to the positive with an increase in concentration of solution and constant current. In sodium sulphate, the spectrum goes through nearly the whole series of spectrograms, and it is found that the maximum relative intensity of the negative to the positive bands occurs at a concentration when the sodium and oxygen spectra have reached their maximum intensity. Consequently, the behaviour of the negative bands is strikingly similar to that of the oxygen elementary line-spectrum. The same conditions are not required for each. In sodium sulphate it was found that the nitrogen spectrum was produced only in a region remote from the point, while the oxygen spectrum is produced only in a region close to the point. In general, the nitrogen band spectra are produced remote from the point in the negative brush and close to the point in the positive brush. There are one or two exceptions in both cases. In distilled water, the bands stretch out from the point with diminishing intensity.

No bands occur in zinc sulphate. In magnesium sulphate, the positive bands occur in the negative brush faintly in one case; the negative bands are absent.

No trace of the nitrogen line-spectrum appears in any of the photographs.

### *Impurities.*

Besides nitrogen, the impurities which yield spectra are calcium, sodium, silicon, and lead. They appear in the

negative brush only. Calcium and sodium are strongest quite close to the point. In the case of a decayed point the calcium lines (notably H, K, and *g*) and the sodium D line are the only lines that occur right up to the point (see fig. 6 *b*). They are probably due, to some extent at least, to the calcium and sodium in the glass which is used in the construction of the point. The silicon lines, which occur chiefly in the far ultra-violet, are often much stronger than the neighbouring platinum lines and occasionally much weaker. It is impossible to predict when and in what strength they will appear, beyond the facts that they are weakest in distilled water and that they never occur at the positive point. In one case, where a quartz platinum instead of a glass platinum point was used, the ultra-violet *band* spectrum of silicon, discovered by de Gramont & Wattville\*, was observed. Only a few of the fainter bands were missing. The lead spectrum, nearly all the lines being in the ultra-violet, was observed in the case of acids. The lines present were those shown by Exner & Haschek to be very powerful in the arc†. They also occur in the flame spectrum, but the bands characteristic of the flame spectrum were absent in that of the brush (Pl. XI. fig. 6).

#### *Acids.*

Of the acids I have tried, hydrochloric and nitric acids have no effect on the spectrum as far as their constituents are concerned. In sulphuric and phosphoric acids there occurs in the discharge a luminous bubble which yields a spectrum connected in all probability with sulphur and phosphorus respectively. In chromic and molybdic acids the spectra of chromium and molybdenum occur at both points. The same remarks apply to the salts of these acids as far as the acid radicle is concerned.

#### *Summary.*

The series and secondary spectrum of hydrogen are a great deal brighter in distilled water than in solutions, for the same current value. In distilled water they are stronger in the negative brush than in the positive for the same current. When the potential drop through the brush is the same in each case,

\* *Comptes Rendus*, vol. cxlvii. p. 239 (1908).

† Kayser's *H. der Spectroscopie*, vol. vi. p. 268.

the spectra are strongest in the positive brush. In solutions, the intensity of the spectra relative to the rest of the brush spectrum (water-vapour bands, platinum and oxygen lines, &c.) is considerably diminished. Neither the nature of the solution nor the sign of the brush has any perceptible effect. There is no certain indication that electrolysis plays any part in the appearance of the spectra.

The spectrum of the metallic lines of the solute appear in the negative brush in solutions. For constant current, the spectrum grows in intensity with the concentration till a certain value of the concentration is reached when no further increase occurs. The spectrum appears in the case of the positive brush in the strongest solutions, and then only very faintly. The behaviour of the spectrum in all cases can readily be explained from the point of view of electrolysis.

The elementary line-spectrum of oxygen appears in distilled water in both the positive and negative brush. In dilute acids, solutions of magnesium and zinc sulphates, and in tap-water, it appears in strength in the positive brush, but is generally absent or very weak in the negative. In solutions of the salts of lithium, sodium, and potassium, its appearance in the positive brush is the same as for other solutions; in the negative brush the spectrum appears with the metallic lines of the salt, increases in intensity with them and reaches its maximum with the same concentration of solution. The negative bands of nitrogen behave in the same manner. In the negative brush, both the positive and negative bands appear in general remote from the point, while the oxygen lines are always produced close to the point.

The arc spectrum of platinum appears in the negative uncondensed brush. In the condensed brush, the spark lines appear. When copper wire is used in the point electrode, the copper lines appear in each brush but are strongest in the negative.

The water-vapour bands appear in each brush equally well.

In conclusion, I wish to thank Prof. Sir J. J. Thomson for the kind interest shown during the prosecution of this research.

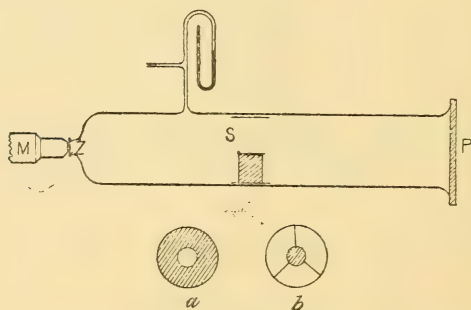
Cavendish Laboratory,  
Cambridge, 1914.



XCI. *The Passage of  $\alpha$  Particles through Hydrogen.* By E. MARSDEN, *Lecturer in Physics, University of Manchester*\*.

ON the nucleus theory of an atom †, Sir Ernest Rutherford and C. G. Darwin have recently discussed the relative motions of an  $\alpha$  particle and the nucleus of an atom in an intimate collision. In the case of the encounter of an  $\alpha$  particle of velocity  $V$  with the nucleus of a hydrogen atom, if the latter is projected in a direction making an angle  $\theta$  with the original direction of the  $\alpha$  particle, then the velocity of the "H" particle is given by  $u = 1.6 V \cos \theta$ . From Bohr's ‡ formula for the "velocity curve" of a charged particle, it can be deduced that in an end-on collision, i. e.  $\theta = 0$ , the "H" particle will have about four times the range of the  $\alpha$  particle producing it. Consequently, in the passage of  $\alpha$  particles through hydrogen the "H" particles may be looked for well beyond the range of the ordinary  $\alpha$  particles, and in the experiments to be described evidence of their existence has been found. More detailed experiments are in progress to investigate whether the distribution of their velocities and relative motions with regard to the  $\alpha$  particles producing them is in agreement with the calculations from the simple assumptions; but, owing to the probable lengthy series of observations necessary, it appears advisable to publish a preliminary account of the experiments so far made.

Fig. 1.



The apparatus used in the first experiments is shown in fig. 1, and consists of a wide tube about one metre in length and 9 cm. in diameter, closed at one end by a zinc-sulphide screen Z and at the other by a glass plate P on a ground flange. A

\* Communicated by Sir E. Rutherford, F.R.S.

† E. Rutherford, *Phil. Mag.* xxi. p. 699 (1911); *Phil. Mag.* xxvii. p. 488 (1914). C. G. Darwin, *Phil. Mag.* xxvii. p. 499 (1914).

‡ N. Bohr, *Phil. Mag.* xxv. p. 10 (1913).

source of about 25 millicuries of radium emanation contained in an  $\alpha$ -ray tube was mounted inside a sheet-iron cylinder so that it could be moved along the tube by a hand electro-magnet.

The tube was filled with hydrogen at atmospheric pressure, and scintillations counted on the zinc-sulphide screen for different distances between S and Z.

The following numbers were obtained :—

Distance of $\alpha$ -ray tube to screen Z.	Scintillations per minute.
24 cm. ....	End of range of $\alpha$ particles.
38 „ ....	10.0 per minute.
50 „ ....	5.5 „ „
82 „ ....	0.5 „ „

With air at a pressure adjusted to give the same range of the  $\alpha$  particles, *i. e.* about 17 cm. Hg, the number of scintillations decreased very rapidly after the end of the range, falling to 0.5 per minute at 26 cm. The results show that in hydrogen, particles capable of producing scintillations are produced which can travel at least  $3\frac{1}{2}$  times as far as the  $\alpha$  particles. That these particles are actually generated in the hydrogen is shown by the following experiment :—A similar iron cylinder to the one carrying the source was placed inside the tube between S and Z. Over the end of this cylinder sheets of aluminium equal in stopping power to 8 cm. of air were fastened. The distance SZ was 17 cm., and by manipulation of a hand electromagnet the foils could be placed either near to the source S or the screen Z. In the former case the  $\alpha$  particles were altogether absorbed by the aluminium and did not emerge into the gas beyond. The following results were obtained :—

Tube.	Al foils.	No. of Scintillations per minute.
Exhausted to 1.5 cm. Hg ...	Near Z	0.7
Hydrogen at 76 cm. Hg ...	„ „	7.75
„ „	Near S	0.13

A comparison of the numbers shows that practically all the scintillating particles originate in the passage of the  $\alpha$  particles through the hydrogen. The small number obtained with the aluminium foils near S only corresponds to one scintillation in 8 minutes, and may be due to natural activity.

The following experiment was made to throw some light on the direction of projection of the H particles. The source was placed about 38 cm. from the screen, and between them at a distance 16 cm. from the source was placed a cardboard stop with a hole 3.2 cm. diameter at the centre (fig. 1 *a*). With this arrangement 6.5 scintillations per minute were observed on the screen. Replacing this stop by its complement a disk 3.2 cm. diameter suspended centrally by threads (fig. 1 *b*), the number was only 2.5 per minute. When an aluminium foil, equal in stopping power of  $\alpha$  particles to 4 cm. of air, was placed near the zinc-sulphide screen, these numbers were reduced to 4.3 and 0.42 scintillations per minute, *i. e.* to 65 and 17 per cent. respectively. In the second case, the relative angles between the H particles and the  $\alpha$  particles will be much greater than in the first case; and the experiment shows, in agreement with theory, that they have a considerably smaller average velocity and are consequently more easily absorbed.

#### *Experiments at High Pressure.*

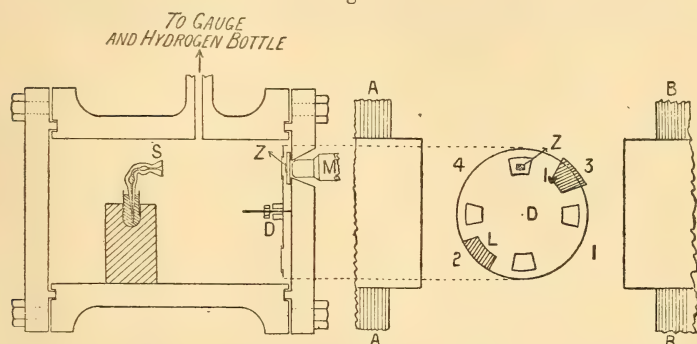
The scintillations produced by the H particles differ little from those produced by  $\alpha$  particles except that they are not so intense. In the above experiments, however, the luminosity of the screen due to the  $\beta$  and  $\gamma$  rays from the source was considerable. Further, the counting was made more difficult owing to the small rate at which the H particles could be made to strike the screen, due to the large distance of the source necessitated by the long range of the  $\alpha$  particles. Experiments were therefore made in hydrogen at high pressure so that the  $\alpha$  particles had a smaller range, and by placing the apparatus in a strong magnetic field the  $\beta$  rays were prevented from striking the screen. The apparatus\* used is shown in fig. 2.

$\alpha$  particles from the source S were absorbed in the hydrogen filling the apparatus, and the H particles produced passed through a hole in the disk D and impinged on a zinc-sulphide screen Z, where the scintillations were observed by

\* The high pressure apparatus was purchased out of part of a grant from the Royal Society.

a microscope M. The source consisted of radium emanation in a conical tube with a thin mica window. The tube was not sealed off, but its end dipped into a small vessel of mercury which also extended into the tube, so as to confine

Fig. 2.



the emanation in a volume at atmospheric pressure about four times the volume of the conical portion of the tube. In this way, when the pressure was raised to about four atmospheres, the emanation just filled the cone and the  $\alpha$  particles were fired through the mica window. The disk D had four openings, three of which were covered with foils of the metal whose absorption was under investigation. A piece of soft iron I was soldered to the disk and nearly counterpoised by a piece of lead L. Thus by the attraction of I, any of the four openings could be brought at will over the zinc-sulphide screen by a cycle of operations of short-circuiting in turn the coils A and B of the electromagnet, the successive positions of I being denoted by 1, 2, 3, 4 in the figure.

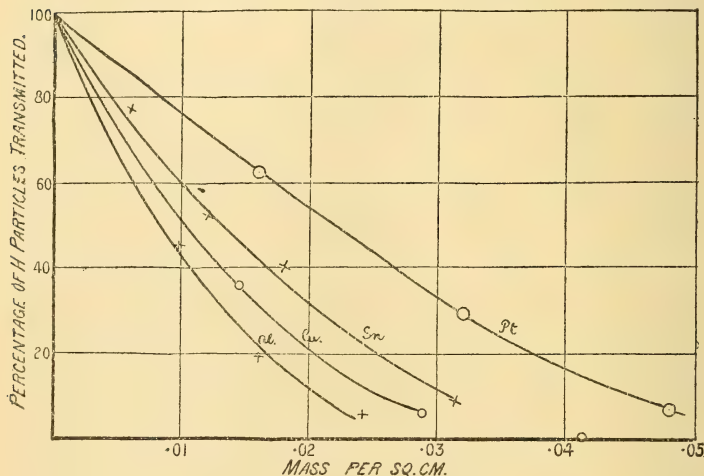
In an experiment the source and disk were first placed in position and the end plates screwed on to the lead joints. The vessel was then swept clear of air by hydrogen from the high-pressure bottle. The valve was then closed and the hydrogen let in gradually until the pressure was about 4.5 atmospheres, this pressure being nearly 0.75 of an atmosphere greater than was necessary to just prevent the  $\alpha$  particles reaching the zinc-sulphide screen.

After four hours the emanation had attained equilibrium with its products on the walls of the conical tube, and observations of the scintillations were commenced. Several hundred scintillations were counted in each of the four positions of the disk, *i. e.* with no foil over the screen and



with foils of different thicknesses over the remaining three openings. The rates at which the scintillations appeared with the different foils were expressed as percentages of the number with no foil, and a curve plotted with these percentages as ordinates and thicknesses of foils as abscissæ. Curves obtained for aluminium, copper, tin, and platinum under the same circumstances are shown in fig. 3.

Fig. 3.



The H particles striking the screen will under the experimental conditions have widely differing velocities, and the foils will act by cutting out the ones with the smallest velocities. It will be noticed, however, that for the same mass per unit area, aluminium shows the greatest percentage absorption of the H particles. This is similar to the law of absorption of  $\alpha$  particles, and further, as with  $\alpha$  particles, the amounts of the various materials required to produce the same absorption are roughly proportional to the square roots of the atomic weights. This is shown by the figures in the following table. The numbers in Col. IV. are obtained from the curves in fig. 3.

The determination of the exact ranges of the swiftest H particles will need more observations than are shown in the figure, but the points where the curves cut the axis of abscissæ give approximate estimates. The most penetrating H particles will be those which are produced by an end-on collision of an  $\alpha$  particle of radium C just after emergence from the mica window, for such an  $\alpha$  particle will be the swiftest entering the hydrogen. The mica had an equivalent

of 1.9 cm., so that the range in air of the  $\alpha$  particle after passing through the window was  $6.9 - 1.9 = 5.0$  cm.; and according to theory\*, if  $\alpha$  particles and H particles of the same velocity are

Foil.	Atomic Weight $A$ .	$\sqrt{A}$ .	Wt. per cm <sup>2</sup> required to reduce beam to 40 p. c. = $W$ .	$W \div \sqrt{A}$ .
Aluminium ...	27.1	5.2	.0108	$2.1 \times 10^{-3}$
Copper .....	63.6	8.0	.0132	1.65 „
Tin .....	119	10.9	.0180	1.65 „
Platinum .....	195.2	14.0	.0266	1.9 „
			Mean	$1.8 \times 10^{-3}$

absorbed similarly, the swiftest H particle produced as above ought to have a range equivalent to about  $4 \times 5.0 = 20$  cm. of air. The hydrogen between the screen and source was calculated from Taylor's† results to have an air equivalent of 7.0 cm., leaving 13 cm. an equivalent for the swiftest H particle. Although the air equivalent of metal foils varies somewhat with the velocity of  $\alpha$  particles and therefore presumably for H particles, we may take for the sake of comparison the weights per unit area per cm. air equivalent given by Richardson‡ and the author for  $\alpha$  particles 6 cm. from the end of their range. Multiplying these numbers by 13 we obtain 0.021 gm. Al, 0.029 gm. Cu, 0.041 gm. Sn, 0.055 gm. Pt. As will be seen from fig. 3 these numbers are not very different from the amounts of the various substances required to completely absorb the H particles, and the agreement verifies the fundamental assumptions made.

The foregoing method is somewhat unsuitable for a determination of the number of H particles produced by a given number of  $\alpha$  particles of known velocity, since  $\alpha$  particles of all velocities are present, and further, the minimum velocity at which a H particle will produce a visible scintillation is a matter of conjecture. However, the number actually observed was about that to be expected from calculations on Darwin's formula, making reasonable assumptions for the difference between the theoretical and experimental conditions.

\* Darwin, *loc. cit.*

† T. S. Taylor, *Phil. Mag.* xxvi. p. 402 (1913).

‡ Marsden & Richardson, *Phil. Mag.* xxv. p. 184 (1913).

A more convenient method of making a comparison between theory and experiment is furnished by the use of a thin film of some substance rich in hydrogen, such as paraffin wax or indiarubber. When  $\alpha$  particles fall on such films, H particles may be expected to be ejected, and experiments have shown that this is actually the case. The observations are at present being continued so as to study the distribution and number of ejected H particles when a parallel beam of  $\alpha$  particles of known velocity passes through these films.

In conclusion I beg to express my indebtedness to Mr. W. C. Lantsberry for his very efficient help in many of the observations, and to Sir Ernest Rutherford for his many kind suggestions.

Physical Laboratories,  
University Manchester.

XCII. *The Magnetic Properties of a Graded Series of Chrome Steels at Ordinary and Low Temperatures.* By MARGARET B. MOIR, M.A., B.Sc., Carnegie Research Fellow in the University of Glasgow\*.

THE influence of temperature upon the magnetic properties of iron, steel, nickel, and cobalt has been investigated by numerous experimenters, perhaps the most notable work being that carried out by Rowland †, Baur ‡, and Hopkinson §.

It is now well known that the effect of raising the temperature of a specimen of iron or steel is to increase its susceptibility to magnetism for low values of the magnetizing force and to diminish it for high values. It is to be expected then that, if the temperature of a test-piece be lowered, the effect should be exactly reversed, and the susceptibility should be diminished for low and augmented for high fields. That such is actually the case has been shown for various magnetic materials by Honda and Shimizu ||, and more recently by Gray and Ross ¶, who have all used the temperature of liquid air,  $-190^{\circ}$  C., as the low temperature at which they have made their investigations. They have shown also that, while alike in this one respect, different materials differ very considerably both in the amount of

\* Communicated by Professor A. Gray, F.R.S.

† Phil. Mag. xlvii. p. 321 (1874).

‡ Wied. Ann. xi. p. 394 (1880).

§ Proc. Roy. Soc. xlv. p. 318 (1889).

|| Phil. Mag. x. p. 548 (1905).

¶ Trans. Faraday Soc. vol. viii. part i. (1912).

change in susceptibility brought about by the change of temperature, and in the value of the field-strength for which the effect reverses its sign.

Now, in any such examination, particular interest always attaches to the observation of the effect of similar treatment on the different members of a graded series, either of steels or alloys, the changes in effect being directly due to the changes in the content of the specimens under examination.

I accordingly decided to examine magnetically a specially prepared series of cobalt-manganese alloys, containing respectively 5, 10, 15, 20, 25, and 30 per cent. manganese, the rest of the content of the specimen being pure cobalt. The proper proportions of the two elements forming the various specimens were therefore weighed out, and sent to be fused and cast, and a specimen of pure cobalt was obtained for comparison. At this point, however, an unexpected difficulty was met with, which ultimately led to the abandonment, for the time being at any rate, of the investigation of this series. It was found that all the ordinary methods which are usually successful in fusing metals were, in the case of the first specimen of the series, ineffectual. It was probable that those specimens with higher percentages of manganese would fuse more easily, but as it was desired to have the complete series prepared by the same method, they were not attempted, and as any other methods which might have been tried were unlikely to give homogeneous alloys, the examination of this particular series had to be abandoned. I therefore decided to investigate instead the magnetic properties at ordinary and low temperatures of a graded series of chrome steels. Such a series was accordingly obtained from Messrs. Armstrong, Whitworth & Co., Ltd.,—a series consisting of six specimens containing respectively 1, 4·05, 8, 12, 16, and 20 per cent. chromium.

The specimens were supplied in the form of cylindrical rods 20 cm. long and 0·9 cm. in diameter, and the conditions in which they were tested were as follows:—

1. As supplied (viz., forged and rolled).
2. Annealed from 900° C.
3. Quenched from 900° C.

In the first condition the specimen is in a state of internal strain brought about by the treatment to which it has been subjected in the course of preparation, and is in general far from homogeneous. Each specimen in this condition was tested magnetically in a Gray-Ross magnetometer, and then changed end for end, and tested again. The two sets of

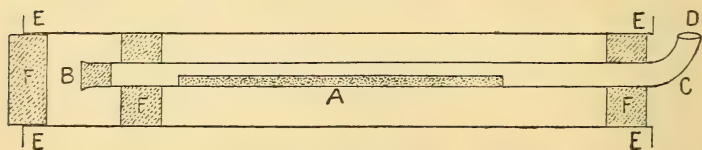


readings in each case were found to differ appreciably, thus showing the want of homogeneity of the specimen. The results of the tests carried out with the specimen in this condition are therefore of comparatively little importance, and are not included in the tables of results.

The effect of annealing the specimen from  $900^{\circ}\text{C.}$  is to remove the internal strains, and bring it into a standard homogeneous condition. In annealing the specimens, a Fletcher gas-furnace, capable of giving temperatures up to  $900^{\circ}\text{C.}$ , was used, and each specimen, before being placed in the furnace, was carefully wrapped in copper foil to exclude air and prevent oxidation.

Each specimen after being annealed was tested magnetically in the usual way, and was then, as before, changed end for end and the test repeated. In the case of each specimen the two tests gave identical results, showing that the material was now homogeneous. The specimen was next immersed in liquid air and tested at the temperature  $-190^{\circ}\text{C.}$  To bring the specimen to that temperature the arrangement shown in fig. 1 below was employed. The

Fig. 1.



specimen A was enclosed in a glass tube BCD, of which the end B was closed with a cork and the end D was open and bent up. Cork bungs F, F were fitted on the tube so as to bring the axis of the specimen into coincidence with that of the solenoid EE, inside which the tube was slipped. A third bung F, or a pad of cotton-wool, was used to prevent access of warm air into the interior of the solenoid, and a covering of cotton-wool wound closely round the tube prevented conduction of heat to the specimen. The liquid air was poured in at the bent end of the tube D, and the specimen kept completely immersed in it for long enough to ensure its temperature being reduced to  $-190^{\circ}\text{C.}$  before a magnetic test was made.

In order to make quite certain that the specimen was in exactly the same position when tested at room-temperature and at the temperature of liquid air, it was inserted in the tube before the test at room-temperature, and not moved between that test and the test at  $-190^{\circ}\text{C.}$  The specimen

was then allowed to heat up to  $15^{\circ}$  C. again, and tested once more to find whether the lowering of the temperature had had any permanent effect upon its susceptibility or not. In addition to the tests already mentioned, each specimen was also tested both at  $15^{\circ}$  C. and at  $-190^{\circ}$  C. for magnetic hysteresis, and the effect of the lowered temperature upon the residual magnetism and the coercive force noted.

The next condition, condition 3, was attained by heating the specimen to  $900^{\circ}$  C. and plunging it into water at  $15^{\circ}$  C.; and with the specimen in that condition, exactly the same series of tests was gone through as in the case of the specimen in the annealed condition. Each complete test was in every case carried out twice, and excellent agreement was obtained between the two sets of results.

One precaution that was carefully observed in the carrying out of this work is to be specially noted. After every change of temperature, and before a magnetic test was made at the new temperature, the specimen was subjected to a process of demagnetization by reversals which, the initial value of the field being great and the final value zero, left it devoid of magnetism and magnetic history. It is well known that some such process must be applied to a specimen previous to carrying out a magnetic test in order that it may be rendered neutral; but it is far from generally known that any thermal treatment applied to a specimen between its neutralization by the process of reversals and the following magnetic test, renders it peculiarly susceptible to magnetism\*, and that therefore a specimen rendered neutral at one temperature ceases to be neutral if the temperature is changed. Before carrying out a magnetic test after a change of temperature then, it is essential that the specimen should be submitted to a process of reversals *at the new temperature*.

#### DISCUSSION OF RESULTS.

*Specimen I. (1 per cent. Cr.).*—The first specimen tested was a steel containing 1 per cent. chromium. The chief results obtained are shown in Table I., and the corresponding curves in fig. 2. The first set of results, corresponding to the curve marked I, gives the readings for the I-H curve taken with the specimen at room-temperature in the annealed condition. The corresponding curve marked I' belongs to the second set of results, and is the curve characteristic of the annealed specimen at the temperature of liquid air.

\* "On Magnetic Testing," by J. G. Gray & A. D. Ross, *Phil. Mag.* Jan. 1911.

TABLE I. (Fig. 2.)

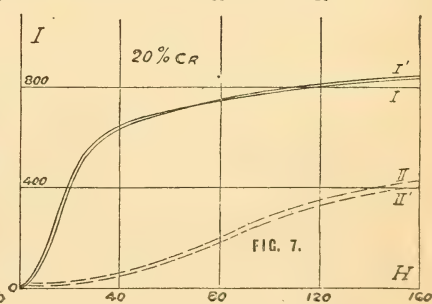
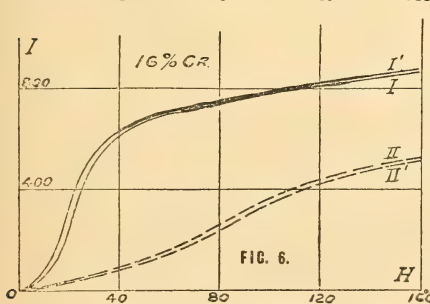
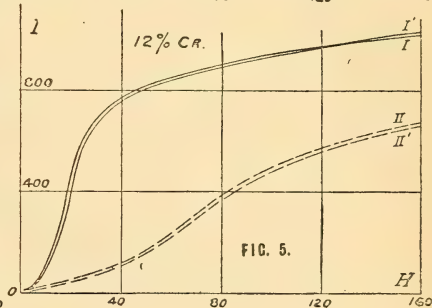
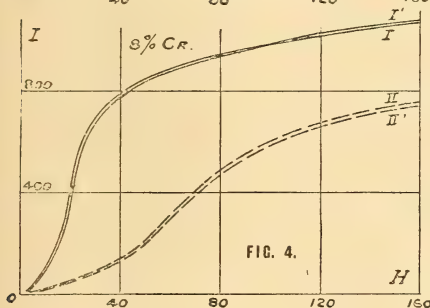
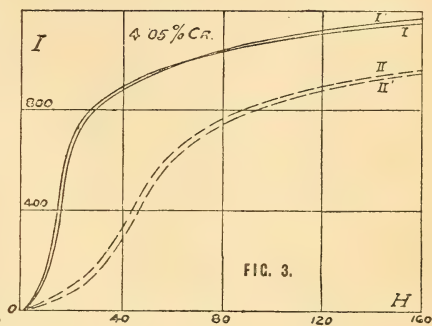
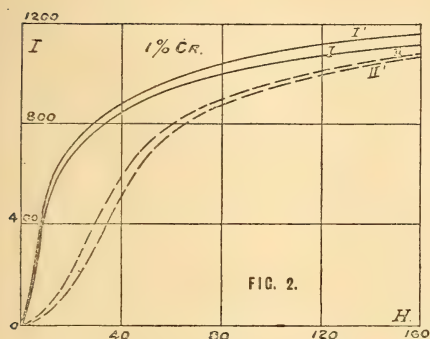
1 per cent. Cr.

Thermal treatment .....	Annealed at 900° C.		Quenched at 900° C.	
Temperature of test.....	15° C.	-190° C.	15° C.	-190° C.
H.	I.	I.	I.	I.
5	190	130	16	10
10	460	480	60	40
20	680	708	210	143
40	844	878	588	504
60	940	978	796	762
100	1040	1082	960	944
150	1117	1159	1076	1060

It is to be noticed that this latter curve starts below the former, as was to be expected, but crosses it very early in the range, the value of the magnetizing force at the crossing-point being only about 8 c.g.s. units. Thereafter the curve at  $-190^{\circ}\text{C.}$  lies entirely above the curve taken at room-temperature, and the improvement in magnetic quality becomes more marked as the field is increased in value. The results of the next test, made after the specimen had again reached room-temperature, are not included in the table nor in the diagram. The curve belonging to this test, however, almost coincides with the previous curve taken at room-temperature, lying only very slightly below it at the beginning of the range and slightly above it later on, the crossing of the curves in this case also being in the neighbourhood of  $H=8$ . That is to say, the effect on the specimen of immersion in liquid air is to give it a permanent set magnetically in the direction of its condition at  $-190^{\circ}\text{C.}$  The change in susceptibility is, however, very small.

The other two curves, the dotted curves marked II and II', belong to tests 3 and 4 in Table I., and show the results obtained on testing the specimen in the quenched condition. II is the curve taken at ordinary temperature, II' is the curve belonging to  $-190^{\circ}\text{C.}$  In this case the liquid-air curve lies everywhere below the curve taken at room-temperature, and the form of the curves shows that crossing will only occur for a very high value of the magnetizing force. The third test, made when the specimen had again reached room-temperature, gives a curve which exactly coincides with curve II, showing that in the quenched condition the lowering of the temperature of the specimen to  $-190^{\circ}\text{C.}$  does not permanently affect its magnetic quality.

The general effect of quenching on the specimen is to diminish its susceptibility, particularly for low and moderate fields.



— SPECIMEN IN ANNEALED CONDITION  
 - - - - - " " QUENCHED  
 I & II TESTED AT ROOM TEMPERATURE  
 I' & II' " " -190° C.

Some of the hysteresis curves obtained for this specimen are shown in fig. 8. The curves marked I and I' are, as before, the curves obtained on testing the specimen in the annealed condition at 15° C. and -190° C. respectively.



It will be noted that for low fields the curves are coincident, though for higher fields I' lies above I. The residual magnetism at both temperatures is about 400 c.g.s. units, and the coercive force about 5 c.g.s. units. The dotted

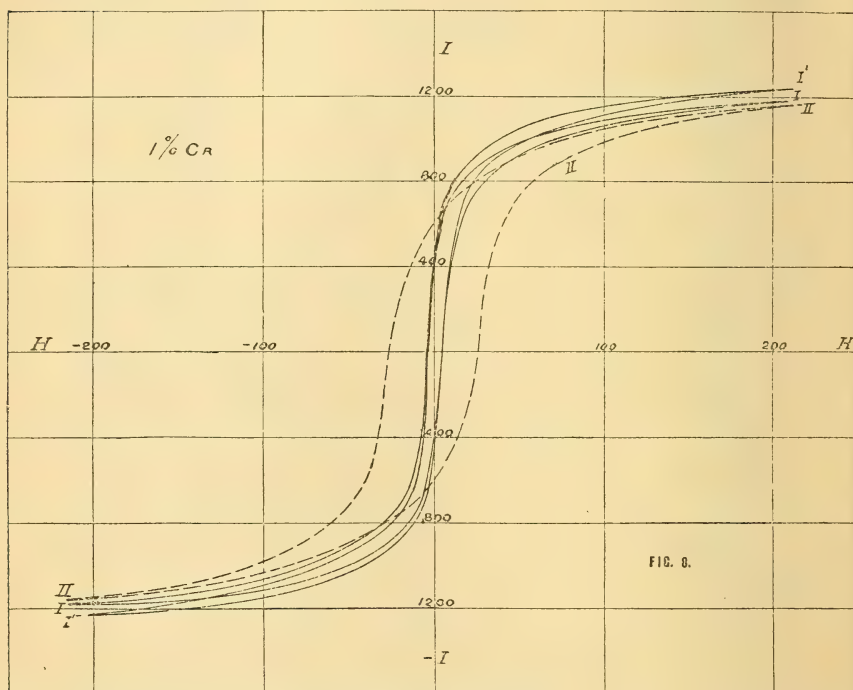


FIG. 8.

curve marked II is the hysteresis curve of the quenched specimen at  $15^{\circ}\text{C}$ . To prevent confusion of the diagram, the curve taken at  $-190^{\circ}\text{C}$ . is not shown, but it very nearly coincides with II. The values of the residual magnetism at  $15^{\circ}\text{C}$ . and  $-190^{\circ}\text{C}$ . are respectively 600 and 605 c.g.s. units, and the values of the coercive force 28 and 33 c.g.s. units.

*Specimen II. (4.05 per cent. Cr.).*—The results obtained on testing this specimen are contained in Table II. These readings and the corresponding curves of fig. 3 show that this specimen is magnetically very similar to the previous one except in one or two points. As before, the curve taken at  $-190^{\circ}\text{C}$ ., when the specimen is in the annealed condition, starts below and finishes above the curve taken at  $15^{\circ}\text{C}$ ., but in this case the crossing occurs for a much higher field value,

TABLE II. (Fig. 3.)

4.08 per cent. Cr.

Thermal treatment .....	Annealed at 900° C.		Quenched at 900° C.	
Temperature of test.....	15° C.	-190° C.	15° C.	-190° C.
H.	I.	I.	I.	I.
10	160	125	38	24
20	680	608	95	68
40	892	878	317	270
60	980	970	630	590
100	1078	1088	840	820
150	1142	1158	945	935

namely 70 c.g.s. units. The curve taken at room-temperature after the test at  $-190^{\circ}\text{C}$ . is again slightly below I at the beginning of the range and slightly above it at the end, but the improvement only sets in when the field is greater than 110 c.g.s. units. The effect of quenching in reducing the susceptibility of this specimen is more marked than in the case of the previous specimen, but the effects of lowering the temperature after quenching are exactly similar in the two cases,—the curve taken at  $-190^{\circ}\text{C}$ . lying everywhere below that taken at room-temperature, and the two curves taken at room-temperature, the one before and the other after immersion in liquid air, exactly coinciding.

*Specimen III.* (8 per cent. Cr.).—The results obtained on submitting this specimen to the various tests (see Table III. and fig. 4) were again somewhat similar, but the saturation

TABLE III. (Fig. 4.)

8 per cent. Cr.

Thermal treatment .....	Annealed at 900° C.		Quenched at 900° C.	
Temperature of test.....	15° C.	-190° C.	15° C.	-190° C.
H.	I.	I.	I.	I.
10	88	78	18	17
20	400	340	48	42
40	790	778	130	120
60	888	878	304	286
100	984	980	600	580
150	1060	1070	744	724

value of the intensity was found to be lower than previously, and the effect of quenching even more marked than before. The crossing of the curves at the two temperatures in the annealed state occurs at a field value of 102 c.g.s. units, and the magnetic quality at  $15^{\circ}\text{C.}$ , after immersion in liquid air, is lower than before immersion for fields less than 170 c.g.s. units. An examination of this specimen when quenched produced exactly the same results as in the previous cases—that is to say, the magnetic quality when the temperature is lowered to  $-190^{\circ}\text{C.}$  is less than at room-temperature for the whole range examined, and returns to its original value when the temperature is allowed to rise again.

*Specimens IV., V., and VI. (12 per cent. Cr., 16 per cent. Cr., and 20 per cent. Cr.).*—The next three specimens showed on examination no marked peculiarities, so I shall not discuss them separately. The results obtained on testing them are exhibited in Tables IV., V., and VI., and the corresponding

TABLE IV. (Fig. 5.)  
12 per cent. Cr.

Thermal treatment .....	Annealed at $900^{\circ}\text{C.}$		Quenched at $900^{\circ}\text{C.}$	
Temperature of test .....	$15^{\circ}\text{C.}$	$-190^{\circ}\text{C.}$	$15^{\circ}\text{C.}$	$-190^{\circ}\text{C.}$
H.	I.	I.	I.	I.
10	80	70	20	13
20	440	380	45	36
40	765	750	112	100
60	850	840	235	210
100	936	932	485	470
150	1008	1018	653	638

TABLE V. (Fig. 6.)  
16 per cent. Cr.

Thermal treatment .....	Annealed at $900^{\circ}\text{C.}$		Quenched at $900^{\circ}\text{C.}$	
Temperature of test .....	$15^{\circ}\text{C.}$	$-190^{\circ}\text{C.}$	$15^{\circ}\text{C.}$	$-190^{\circ}\text{C.}$
H.	I.	I.	I.	I.
10	70	55	17	12
20	320	235	41	35
40	635	608	84	76
60	710	695	162	145
100	780	784	360	340
150	850	865	508	492

TABLE VI. (Fig. 7.)

20 per cent. Cr.

Thermal treatment .....	Annealed at 900° C.		Quenched at 900° C.	
Temperature of test .....	15° C.	-190° C.	15° C.	-190° C.
H.	I.	I.	I.	I.
10	122	106	12	12
20	413	380	25	20
40	636	625	50	42
60	700	698	110	98
100	774	782	276	258
150	820	832	404	390

curves are shown in figs. 5, 6, and 7. In the annealed condition the saturation value of the intensity is lower in each specimen than it was in the previous one, and the susceptibility at  $-190^{\circ}\text{C.}$  is less at the beginning and greater at the end of the range than at  $15^{\circ}\text{C.}$ , the crossing occurring for specimens IV., V., and VI. at points corresponding to field values of 125, 95, and 65 c.g.s. units respectively.

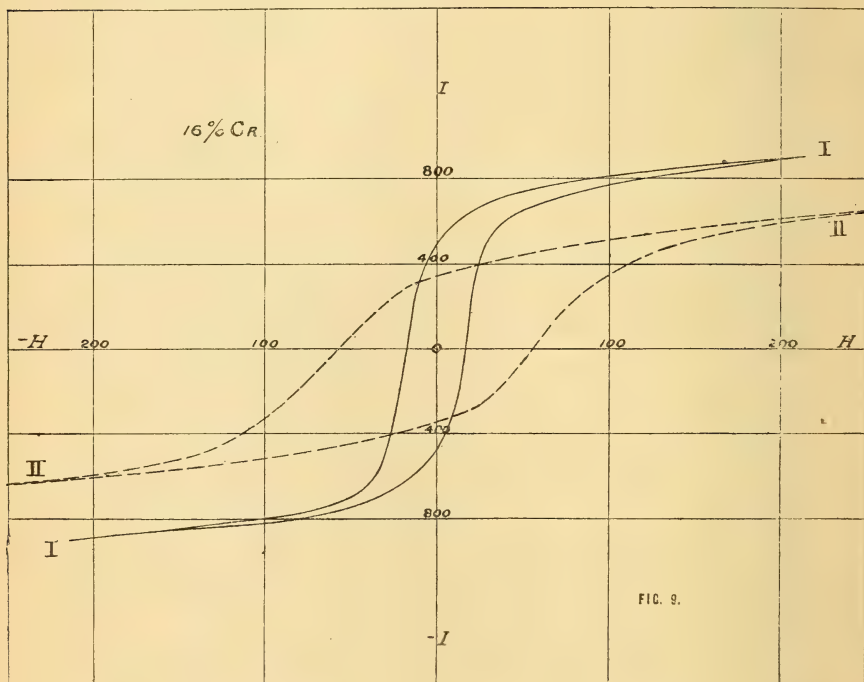
The permanent lowering of the magnetic quality due to immersion in liquid air is seen in these specimens too, the new room-temperature curve lying slightly below the former one for the whole range examined in the case of the specimens containing 12 and 16 per cent. chromium, and till the magnetizing force reaches a value of 90 c.g.s. units in the case of the specimen containing 20 per cent.

In the quenched condition the diminution of magnetic quality with the increase in chrome content is very marked, but otherwise the behaviour of these specimens is exactly the same as that of the three specimens first examined, the curve II' lying invariably below the curve II, and the curve taken when the temperature of the specimen had risen again to  $15^{\circ}\text{C.}$  exactly coinciding with II. For all the specimens, the form of the curves shows that crossing will only take place for very high values of the magnetizing force.

Two of the hysteresis curves for the specimen containing 16 per cent. chromium are shown in fig. 9. These are the curves taken at room-temperature in the annealed and in the quenched conditions. The curves taken at  $-190^{\circ}\text{C.}$  are not shown as they follow almost exactly the lines of those taken at  $15^{\circ}\text{C.}$ , and lie for the greater part of the range just outside them, the residual magnetism and the coercive force both being slightly greater at  $-190^{\circ}\text{C.}$



than at  $15^{\circ}\text{C}$ . The distinctive features of these curves are characteristic in a more or less marked degree of all the specimens of the series, the most notable being probably the extraordinary widening of the hysteresis loop, and the



consequent increase in the coercive force brought about by quenching. The slight improvement in both the residual magnetism and the coercive force, when the temperature is lowered to  $-190^{\circ}\text{C}$ ., is also a characteristic common to all the specimens.

A comparison of these curves with the hysteresis loops for the specimen containing 1 per cent. chromium (see fig. 8) shows that while in the case of the 1 per cent. chromium specimen the residual magnetism is greater in the quenched than in the annealed condition, in the 16 per cent. chromium specimen the reverse is the case. These results are not, however, so irregular as they appear, for as an examination of Table VII. shows, the residual magnetism in the annealed condition increases with increasing percentage of chromium to a maximum value for the specimen containing 8 per cent. and thereafter steadily diminishes, while, in the quenched

condition, the maximum residual magnetism is attained with the lowest percentage of chromium, and every additional amount of chromium produces a diminution in its value. A similar regular change takes place also in the values of the coercive force, but the value in the quenched condition is invariably much greater than the value in the annealed state.

TABLE VII.

	Residual Magnetism.		Coercive Force.	
	Annealed.	Quenched.	Annealed.	Quenched.
1 per cent. Cr. ....	400	660	5	28
4·05 per cent. Cr. ....	500	600	21	39
8 per cent. Cr. ....	660	580	20	46
12 per cent. Cr. ....	510	435	19	54
16 per cent. Cr. ....	490	340	17	56
20 per cent. Cr. ....	440	320	15	44

Coming now to a comparison of the effects produced by lowering the temperature of the different specimens, we find that these effects are on the whole very similar. Considering the quenched specimens first, we see indeed that they behave, so far as the range examined goes, in exactly the same manner, the curve taken at the temperature of liquid air lying in each case below that taken at room-temperature, and the curves taken at room-temperature before and after immersion in liquid air exactly coinciding.

The specimens in the annealed state, however, show some slight differences in behaviour, for while the effect of lowering the temperature to  $-190^{\circ}$  C. is in each case to diminish the susceptibility for low fields and to increase it for high fields, there are considerable variations in the value of the magnetizing force for which crossing of the curves taken at the two temperatures occurs, the actual values of the field-strength corresponding to the crossing point being 8, 70, 102, 125, 95, and 65 c.g.s. units for the specimens containing respectively 1 per cent., 4·05 per cent., 8 per cent., 12 per cent., 16 per cent., and 20 per cent. chromium. As the chrome content increases from 1 per cent. to 12 per cent., that is to say, higher and higher values of the magnetizing force are required to produce crossing of the curves. Further additions of chromium

beyond that point however, tend to lower the position of the crossing point in the range.

In the case of the annealed specimens, again, the effect of lowering the temperature to  $-190^{\circ}\text{C}$ . is not merely a temporary effect which passes away when the temperature is allowed to rise again, but immersion in liquid air produces in the specimen a permanent effect, lowering its susceptibility for low fields and raising it for high, and the crossing points of the two curves taken at room-temperature, one before and one after immersion in liquid air, vary in position exactly as do those of the curves I and I', the crossing for the specimen containing 12 per cent. chromium occurring at a higher point in the range than any of the others.

Briefly, then, the results of this investigation may be summarized as follows :—

(1) The effect of lowering the temperature of a chrome steel is to diminish its susceptibility for low fields and to increase it for high fields.

(2) The crossing of the curves at  $15^{\circ}\text{C}$ . and at  $-190^{\circ}\text{C}$ . in the annealed condition takes place for higher values of the magnetizing force as the chrome content is increased up to 12 per cent., but further additions after that point lower the value of the field for which crossing occurs.

(3) Immersion in liquid air produces a permanent effect on the annealed specimen, which is not wiped out when the temperature is allowed to rise to room-temperature again.

(4) For specimens in the quenched condition the crossing of the curves at  $15^{\circ}\text{C}$ . and  $-190^{\circ}\text{C}$ . occurs for very high values of the magnetizing force, probably much greater than 160 c.g.s. units.

(5) Immersion in liquid air has no permanent effect on quenched specimens ; and

(6) In both the annealed and quenched conditions the residual magnetism and the coercive force are greater at  $-190^{\circ}\text{C}$ . than at  $15^{\circ}\text{C}$ .

In conclusion, I desire to express my thanks to Professor Gray and to Dr. J. G. Gray for the interest they have taken in the progress of the work.

XCIII. *An Experiment indicating that Matter takes up no Room in the Æther.* By C. V. BURTON, D.Sc.\*

1. **I**N a former paper† it was suggested as a possibility that electrically neutral bodies moving through the æther might exert forces on one another in virtue of their motion; and it was shown that such effects were to be expected unless a certain simple condition were fulfilled. Briefly expressed, the condition is that matter should take up no room in the æther, a form of statement which perhaps needs further explanation. When surrounded by the atmosphere, a body impermeable to air is commonly said to displace its own volume of air: the room which the body occupies in the air is positive, and its measure is the volume of the body. Similarly, in complete accordance with the common use of terms, we may say that, in an atmosphere traversed by sound-waves, the rarefactions take up positive and the condensations negative room, the disturbance as a whole taking up no room. Regarding matter and æther, the question may be proposed whether the mean ætherial density is less (greater) in a region where matter is present than in a vacuum, the room which matter takes up in the æther being in that case positive (negative); or whether the presence of matter produces on the whole no modification of ætherial density, so that matter takes up no room whatever in the æther. When it is stated that, within the limits of accidental error, the latter conclusion is supported by the experiment to be described, this is not to be taken as implying that electrons and atomic nuclei are of vanishingly small dimensions, but rather that the modifications of ætherial conditions which constitute these entities are not such as involve, on the whole, any appreciable change of density.

2. The nature of the experiment will be most readily understood in relation to the effects which should have been observed if these had been appreciable. In ordinary hydrodynamics (discontinuities apart) a solid body moving through an unbounded liquid produces at remote points the effect of a doublet; the direction and strength of the equivalent doublet depending not merely on the volume and motion of the body, but on its shape and orientation. The case which we have to consider is somewhat analogous but essentially simpler. Thus "let  $F$  be a physical magnitude characteristic of all electrically neutral matter and defined as follows: If into a

\* Communicated by the Author.

† Phil. Mag. Jan. 1909.



region bounded by a fixed ideal surface and originally free from atomic matter, a mass  $m$  of matter is introduced,  $Fm$  is the volume of æther which flows outward across the bounding surface". If  $\rho$  is the density of the æther, it is the quantity  $F^2\rho$  which should be effective in producing forces between bodies which are in motion through the æther, and from the null result given by the observations an upper limit is assigned to the value of  $F^2\rho$ .

3. This work was undertaken because it seemed by no means self-evident that the property sought for must be absent. If positive results had been obtained, the means of determining our motion with respect to the æther would have been to hand; nor would such a result have been necessarily in contradiction to the electromagnetic principle of relativity, the effects in question being outside the electromagnetic scheme. But since no such effects were observed, those who uphold the principle of relativity in its most absolute sense will find nothing here to impugn their beliefs.

4. It is shown in the sequel that if  $F^2\rho$  were finite, a flat plate moving uniformly in a given direction through the æther would tend to set itself with its plane perpendicular to that direction, being acted on by a couple whenever its normal was oblique to the line of motion†. Accordingly the most convenient way to test for the existence of the effects now in question is to suspend such a plate by a fine fibre so that its plane is vertical, and to watch for any changes of azimuth which may occur as the earth's rotation causes the suspended system to be presented in varying aspects to the earth's line of motion.

#### *Experimental Arrangements.*

5. Observations were made with two different suspended plates, each of 5 per cent. iridio-platinum. The first plate had the form and dimensions indicated in fig. 1. The tail served as a point of attachment for the suspending fibre; it was integral with the plate, and was much thinner than the main portion, one side of which was optically polished. The second plate (fig. 2) was of simple rectangular form, and had near its top end a minute hole through which could be

\* *Loc. cit.*

† There is thus a certain analogy to the case of a laminar solid moving bodily through a frictionless liquid; but the analogy is by no means close. We are here concerned with the actions exerted between the æther and the nuclei and electrons of which a material plate is made up; we suppose that the motion of these through the æther is simply a question of strain-transference, and involves nothing of the nature of a gross bodily displacement.

passed a little platinum hook serving for the attachment of a quartz fibre.

Fig. 1.

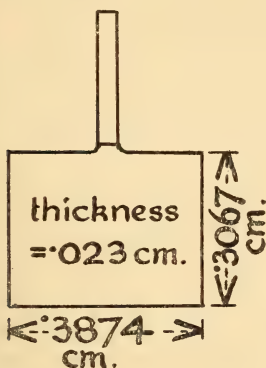
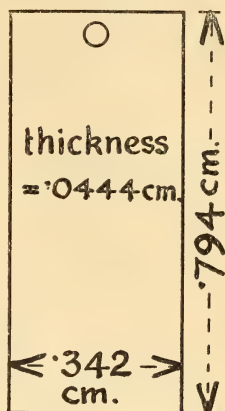


Fig. 2.



6. The attachment of the fibres called for special care, because a gradual drift of "zero," which would be of little consequence in many instruments, might here be a serious trouble. Various forms of soldering were tried, but on the whole the best results were got with comparatively soft cements, such as flexible shellac and a hardish form of adhesive wax. (The quartz fibres were of course allowed to untwist before their ends were cemented.) Though the rate of creep immediately after suspension might then be fairly rapid, in a few days the soaking out of the torsional strains was so far complete that observations could be made and the still continuing creep allowed for. A persistent drift in azimuth taking place in a smooth manner was naturally less objectionable than far smaller changes occurring irregularly; but it was essential that the progressive displacement should not be so rapid as to pass beyond the range of the adjustments in the course of a few days.

7. It was evident from the first that convection currents within the suspension-chamber were likely to be a source of trouble; but it was not practicable to surround the suspended plate by massive metal walls, leaving only a minimum of clearance for free libration; for the gravitational forces exerted on the plate by the walls would then have been relatively large, and minute tilts of the apparatus as a whole, by shifting the position of the plate within the enclosure, would have caused these forces to vary.

8. At the outset it had been intended to exhaust the

suspension-chamber to the highest vacuum obtainable by means of a Töpler pump; but it was very difficult to ensure that the whole was really air-tight; and an air-jet entering at a microscopical leak in some unknown position might well become a source of serious uncertainty, so in the actual observations the plate was surrounded by air at atmospheric pressure. The suspension-chamber was formed of a mild steel tube having an internal diameter of 3.2 cm., with walls about 0.6 cm. thick, and of sufficient height to allow of the use of a suspending fibre 30 cm. long. This tube was hermetically sealed below, and was closed above by an air-tight conical cap. It was provided with a thick window of worked glass, and was fixed by screwing into a large circular cast-iron plate, which in turn was adjustably bolted to the cast-iron bed-plate of the apparatus; the plate also carried a cast-iron cell in which an achromatic object-glass was geometrically seated. As an indication of the precautions taken against convection currents, it will suffice to mention the several protecting shells which would be revealed by a section in a horizontal plane through the suspended plate. Proceeding outwards from the plate, we should encounter first the sides of a box \* measuring about  $1.2 \times 1.2 \times 1.2$  cm., and made of aluminium-foil, with a front of selected microscope cover-slip; then the walls of the steel tube with worked glass in front; then a cylinder of sheet zinc (which had a wooden cover); and finally the sides of a box made of half-inch match-boarding. This last was supported from the cement floor independently of the apparatus, and was closed as completely as possible, only such small apertures being left as were determined by the optical requirements, and by the necessity for keeping the woodwork out of actual contact with the bedplate.

9. The entire apparatus, including the vital parts of the optical system, was firmly clamped upon the bedplate, and this in turn was supported on three steel balls of 1.6 cm. diameter, which were interposed between it and the seating. Of these balls the first had three points of contact with the seating and three with the underside of the bedplate; the second lay between a V-groove in the seating and a similar groove in the underside of the bedplate, these grooves pointing in the direction of the first ball; while the third ball lay between two horizontal plane surfaces, one belonging to the seating and the other to the bedplate. Those parts of the seating which contributed to this double "hole slot and

\* This box contained a trace of uranium oxide, to eliminate variable electrostatic effects.



plane" arrangement were formed of cast iron, and (like the corresponding parts of the bedplate) were machined. They were cemented to stone slabs, carried in turn upon 12-inch socket-drain-pipes which stood vertically upon the cement floor; all contacts being of course "geometric." By the mode of support just described, the position of the bedplate was positively determined, and on the other hand, it was impossible for small movements of the seating (due *e. g.* to temperature changes) to impose any appreciable stresses on the bedplate. Such movements, taking place slowly, might conceivably produce minute tilts or azimuthal displacements of the apparatus as a whole, but the effect of these on the micrometer-readings was not detectable.

10. The optical system used for reading the excursions of the mirror-polished plate has already been described under the name of "micro-azimometer"\*, and need only be briefly referred to here. The arrangement was an auto-collimated one, with an achromatic lens fixed before the window of the suspension-chamber, and a fine vertical illuminated slit in the principal focal plane of the lens. The image of the slit formed by light which had passed twice through the lens, and had been intermediately reflected by the suspended mirror, was viewed through an eyepiece which latterly consisted of a single cylindrical lens (not achromatized) with generating lines vertical. This had a focal length of about 1.5 cm., and the image of the slit thus observed was sufficiently supermagnified to show the diffraction pattern on a fairly open scale. The position of the slit was micrometrically adjustable, and the image could thus be brought into agreement with a fixed vertical wire, upon which the eyepiece was focussed. The thickness of the wire was such that, when the setting was correct, the central band of the diffraction pattern was almost wholly eclipsed, leaving only a narrow residual strip of light visible on either side of the wire. A very slight deviation from central setting caused these residual strips to appear of unequal brightness, so that in favourable circumstances very close settings could be made.

11. Tests were made of the delicacy of the optical system by fixing the little polished plate, and observing how consistently the micrometer controlling the position of the slit could be set and reset. It was thus found that, with the first mirror (fig. 1) and using an ordinary eyepiece, the probable error of a single setting (expressed in terms of the azimuth of the mirror) was rather less than 0.5 second of arc; while with the second mirror (fig. 2) and using a cylindrical lens

\* *Phil. Mag.* March 1912.



as eyepiece, the probable error of a single setting was reduced to 0.05 second.

12. The first plate, when suspended, had a complete torsional period of 8.5 seconds, and the readings obtained were sufficiently consistent to make the full optical sensitiveness significant. The second plate was so suspended as to have a complete torsional period of 58 seconds, and in this case the accidental error was seen to be considerably greater than the error of setting. Everything was done which suggested itself as likely to reduce thermal disturbances within the suspension-chamber; in addition to the successive protecting envelopes already referred to, a stout wooden screen was used to intercept radiated heat from the observer or from the lamp, the source of light being a very small acetylene flame enclosed as completely as was possible, and the slit being of necessity exceedingly narrow. Several stops were also used to ensure that no light outside the limits of the useful beam should reach the suspension-chamber; and finally a shutter was arranged to cut off all light from the apparatus except when the field was being actually observed.

13. It may be remarked that, with such high magnification, and especially when the cylindrical form of eye-lens is used, the demands on the optical quality of the suspended mirror are severe, and the polishing was found very troublesome. The thinness and consequent flexibility of the plate made it necessary to do all the grinding and polishing on dry tools, and considerable practice was needed before the correct manipulation was obtained. The chief difficulty, however, was in testing the figure of the polished or partly polished surface by applying it to a quartz plane; for the plate very readily attached itself limpet-wise to the quartz, its flexibility enabling it to come into close contact, even when the form of the unstrained surface was far from flat. But these difficulties were at length overcome, and satisfactory flatness obtained. The second plate (fig. 2) was the one used in conjunction with a cylindrical eye-lens, and the only defect of figure which it finally showed was such as would have been produced in a naturally flat plate by holding it at top and bottom and minutely wringing it about a vertical axis. This caused the image of a vertical slit (viewed through a cylindrical eye-lens) to be slightly inclined to the vertical; a trouble which is not to be abated by any tilting of the slit, the fiducial wire, or the eye-lens. The difficulty, however, was readily removed by placing close to the object-glass a very weak plano-cylindrical lens which could be turned round in its own plane until the desired compensation was effected.

14. It had been my intention, in case there had been any indication of positive results, to determine the corrections which must be made for possible disturbing influences, especially such as might be suspected of contributing diurnal or semi-diurnal terms to the azimuth of the suspended plate: for example, changes in the temperature of the apparatus, and in the elements of the surrounding magnetic field. Against such disturbances every precaution had been taken at the outset; and when the observations failed to show anything periodic emerging above the accidental errors, it did not seem necessary to consider them further. The experiment indeed was brought to an end by the failure of a suspension, the renewal of which would have involved a considerable expenditure of time; the result to be achieved being in all likelihood only a moderate lowering of the limit given in § 21.

### *Theory and Conclusions.*

15. Before the (null) results of the observations can be discussed, it will be necessary to give an outline of the theory of the experiment, in order to show what should have been observed if  $F^2\rho$  (§ 2) had been great enough to give rise to measurable effects. The starting-point is an equation, numbered (29) in the 1909 paper already cited, and giving the force  $m(X, Y, Z)$  experienced by a material particle of mass  $m$  at  $(x, y, z)$  owing to the motion of another particle of mass  $m'$  at  $(x', y', z')$ . This equation may be written

$$mX = \frac{mm'F^2\rho}{4\pi} \left\{ \left( \frac{9\xi}{r^5} - \frac{15\xi^3}{r^7} \right) \left( \frac{dx'}{dt} \right)^2 + \left( \frac{3\xi}{r^5} - \frac{15\eta^2\xi}{r^7} \right) \left( \frac{dy'}{dt} \right)^2 \right. \\ + \left( \frac{3\xi}{r^5} - \frac{15\xi^2\xi}{r^7} \right) \left( \frac{dz'}{dt} \right)^2 + \left( \frac{6\eta}{r^5} - \frac{30\xi^2\eta}{r^7} \right) \frac{dx'}{dt} \frac{dy'}{dt} \\ + \left( \frac{6\xi}{r^5} - \frac{30\xi^2\xi}{r^7} \right) \frac{dx'}{dt} \frac{dz'}{dt} - \frac{30\xi\eta\xi}{r^7} \frac{dy'}{dt} \frac{dz'}{dt} - \left( \frac{1}{r^3} - \frac{3\xi^2}{r^5} \right) \frac{d^2x'}{dt^2} \\ \left. + \frac{3\xi\eta}{r^5} \frac{d^2y'}{dt^2} + \frac{3\xi\xi}{r^5} \frac{d^2z'}{dt^2} \right\}$$

with similar expressions for  $mY, mZ, \dots \dots \dots$  (1)

where  $\xi, \eta, \zeta \equiv x' - x, y' - y, z' - z$ ; and  $\rho$  is the density of the æther.

16. Suppose, now, that the particles  $m, m'$  are constituents of a body moving through the æther with a velocity  $(U, V, W)$  which may be considered uniform throughout the body; and let the variations of  $U, V, W$  be so slow that terms involving

accelerations may be omitted from the right-hand side of (1). The forces experienced by  $m$  and  $m'$  are then seen to be equal and opposite; taken together they form a couple, whose moment about the  $z$ -axis in the sense  $x$ -axis to  $y$ -axis is

$$mX\eta - mY\xi \\ = \frac{3F^2\rho mm'}{2\pi r^5} [\xi\eta(U^2 - V^2) + (\eta^2 - \xi^2)UV + \xi W(\xi V - \eta W)], \quad (2)$$

in virtue of (1).

17. If we are dealing with a body of uniform density  $\sigma$ ,  $mm'$  must be replaced by  $\sigma^2 dx dy dz dx' dy' dz'$ , and the component turning moment about the  $z$ -axis due to the velocity ( $U, V, W$ ) of the body through the æther has to be found by integration. If the body has the form of a rectangular plate whose edges are parallel to the axes of reference, only those terms of (2) will survive the integration which do not change sign with  $\xi$ , or with  $\eta$ , or with  $\zeta$ ; so that the expression for the turning-moment reduces to

$$UV \frac{3F^2\rho\sigma^2}{2\pi} \iiint \frac{(y-y')^2 - (x-x')^2}{r^5} dx dy dz dx' dy' dz'. \quad (3)$$

Let the edges of the plate be  $a, b, c$ , and let  $b:c$  be small, but  $a:c$  not necessarily small: then the approximate value of (3) is found to be

$$UV \cdot F^2\rho \cdot \frac{M\sigma}{\pi} \left\{ -\pi + 4 \tan^{-1} k + k \log(k^{-2} + 1) - k^{-1} \log(k^2 - 1) \right\}, \quad (4)$$

where  $M = abc\sigma$  (the mass of the body) and  $k = b/a$ . When  $b/c$  is vanishingly small, this expression becomes exact.

18. The turning-moment about the  $z$ -axis exerted upon a rectangular plate such as that now considered takes the form

$$UV \cdot F^2\rho \cdot M\sigma \cdot H, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where  $H$  is a numerical coefficient depending on the ratios  $a:b:c$ . When  $b:c$  is very small, we find from (4)

$b/a$	0	0.1	0.2	1
$H$	1	.7575	.6126	0

The values assumed by  $H$  when  $b:c$  and  $a:c$  are both finite could of course be found, though not necessarily in finite terms. In the actual apparatus  $b:c$  was successively about 1:13 and 1:17, and the table just given provides values abundantly accurate for the purpose in view. It will be noticed that, when the proportions are fixed, the turning-moment due to

given velocity-components  $U, V$  is proportional to the mass and density of the plate conjointly, and the advantage of using a material of high density is thus evident.

19. In the application of the formula (5) to the apparatus used, the axis of  $z$  is vertically upward,  $x$  parallel to the breadth of the plate, and  $y$  parallel to its thickness. Let  $\varpi$  be the angle, reckoned in the sense NESW, which the normal to the face  $ab$  makes with the meridian. While the other factors of (5) remain constant,  $UV$  will vary with the time, and will necessarily involve the unknown velocity of the sun with respect to the æther. As axes fixed in space take

$z'$  in the direction (S to N) of the earth's axis,  
 $y'$  „ „ of the first point of Aries,  
 $x''$  forming a right-handed system with  $y', z'$ ;

(thus at the vernal equinox the axis of  $x$  makes an acute angle with the earth's way). The velocity-terms due to the earth's rotation will here be neglected. Let  $(A, B, C)$  be the velocity of the earth's centre through the æther, referred to the axes of  $x', y', z'$ . Let  $\phi$  be the angle through which the earth has turned since a certain transit of the first point of Aries, and  $\theta$  the co-latitude of the place of observation. We then find

$$\begin{aligned} UV = & \left\{ \frac{1}{4}(A^2 - B^2) \sin 2\varpi(1 + \cos^2 \theta) + AB \cos 2\varpi \cos \theta \right\} \cos 2\phi \\ & + \left\{ \frac{1}{2}AB \sin 2\varpi(1 + \cos^2 \theta) + \frac{1}{2}(B^2 - A^2) \cos 2\varpi \cos \theta \right\} \sin 2\phi \\ & + \left\{ -AC \cos 2\varpi \sin \theta + \frac{1}{2}BC \sin 2\varpi \sin 2\theta \right\} \cos \phi \\ & + \left\{ -BC \cos 2\varpi \sin \theta - \frac{1}{2}AC \sin 2\varpi \sin 2\theta \right\} \sin \phi \\ & + \frac{1}{4}(A^2 + B^2) \sin 2\varpi \sin^2 \theta - \frac{1}{4}C^2 \sin 2\varpi \sin 2\theta. \quad \dots (6) \end{aligned}$$

20. In the actual case,  $\varpi = \pi/4$  approximately, and (6) becomes

$$\begin{aligned} UV = & \frac{1}{4}(A^2 - B^2)(1 + \cos^2 \theta) \cos 2\phi + \frac{1}{2}AB(1 + \cos^2 \theta) \sin 2\phi \\ & + \frac{1}{2}BC \sin 2\theta \cos \phi - \frac{1}{2}AC \sin 2\theta \sin \phi \\ & + \frac{1}{4}(A^2 + B^2) \sin^2 \theta - \frac{1}{4}C^2 \sin 2\theta. \quad \dots (6a) \end{aligned}$$

Here each of the components  $A, B, C$  of the earth's velocity through the æther may be regarded as made up of two terms, one due to the sun's unknown velocity through the æther, the other to the earth's orbital motion. Now the sun's velocity, it may be supposed, does not vary perceptibly in direction or magnitude during the period covered by any practicable observations, and over an interval not exceeding



a few days the earth's orbital velocity may also, with sufficient approximation, be treated as constant in direction and magnitude. Thus at any well-defined time of year the terms in  $\cos 2\phi$ ,  $\sin 2\phi$  which occur in (6a) represent a semi-diurnal constituent of UV, and the terms in  $\cos \phi$ ,  $\sin \phi$  a diurnal constituent; the amplitude of the semi-diurnal term is

$$\frac{1}{4}(A^2 + B^2)(1 + \cos^2 \theta),$$

and that of the diurnal term is

$$\frac{1}{2}\sqrt{(A^2 + B^2)}C \sin^2 2\theta.$$

21. The corresponding amplitudes of the semi-diurnal and diurnal turning-moments about a vertical axis are

$$\frac{1}{4}(A^2 + B^2)(1 + \cos^2 \theta)F^2\rho M\sigma H, \quad . \quad . \quad (7)$$

and  $\frac{1}{2}\sqrt{(A^2 + B^2)}C \sin^2 2\theta F^2\rho M\sigma H, \quad . \quad . \quad (8)$

respectively; and limits can be named which these certainly did not exceed with the apparatus used. In seeking to assign an extreme upper limit to the value of  $F^2\rho$ , we must assume for A, B, C the values least favourable to the production of measurable amplitudes. If a large number of observations were available, well distributed over a year, the most unfavourable assumption would be that the sun was at rest (or nearly so) with respect to the æther. For a single set of observations taken at one time of the year, this assumption would no longer be the most unfavourable; for it might be thought possible that the sun's velocity was equal and opposite to the earth's orbital velocity at the time in question, the earth's centre being then at rest with respect to the æther. All the same, we should be justified in saying that  $F^2\rho$  was *probably* below a certain value, calculated on the supposition that the sun was without motion through the æther.

22. Of the observations taken there are two sets suitable for reduction; one made in 1910 (October 29–31, the other (with considerably greater refinement) in 1913 Feb. 4–10. In the earlier set, the plate shown in fig. 1 was used, and it appeared from a plot of the micrometer readings that the azimuth of the mirror showed no semi-diurnal variation with an amplitude as great as 1.5 seconds. The moment of inertia of the plate being .00076 (c.g.s.) and the period 8.50 seconds, this implies that there is no semi-diurnal couple acting on the plate with an amplitude as great as  $3.15 \times 10^{-9}$  dyne-cm.; that is, in virtue of (7),

$$\frac{1}{4}(A^2 + B^2)(1 + \cos^2 \theta)F^2\rho \cdot M\sigma H < 3.15 \times 10^{-9}.$$

In the left-hand member of this inequality we are certainly justified in taking (A, B, C) to be as great as the earth's orbital velocity, for the adverse chance referred to in § 20 cannot here cast doubt on our conclusions, inasmuch as a null result was also given by the readings of 1913 Feb., in which the fineness of observation was increased tenfold. The value which may be assigned to  $A^2+B^2$  is thus roughly  $(3 \times 10^6 \text{ cm./sec.})^2$ ;  $\theta$  the co-latitude is about  $38^\circ 15'$  or  $1 + \cos^2 \theta = 1.62$ ;  $M = .0616 \text{ gram}$ ;  $\sigma = 21.6$ ;  $H$  (§ 18) is not less than .75. Hence

$$F^2 \rho < 10^{-21} \text{ certainly.}$$

23. The second set of observations used was made with the plate shown in fig. 2; and if there were any semi-diurnal term in the azimuth of the mirror, the amplitude was certainly less than 8 seconds. The moment of inertia of the plate was .00258 c.g.s., and its period 58 seconds, so that there was no semi-diurnal couple acting on the plate with an amplitude as great as  $1.36 \times 10^{-9} \text{ dyne-cm.}$  Proceeding as in § 22, with the probable assumption that the quadratic velocity-factor  $A^2+B^2$  is at least that due to the earth's orbital motion, we find that

$$F^2 \rho < 10^{-22} \text{ probably.}$$

24. Let us now provisionally assume for the density of the æther the value  $10^{12} \text{ grams per c.c.}^*$  From the result of § 22 it would then follow that  $F^2 < 10^{-23}$ , and that  $F$  (whether positive or negative) is numerically less than  $3.1 \times 10^{-17}$ , a limit which is depressed to  $10^{-17}$  if we assume the result given as probable in § 22. Thus, if  $\rho = 10^{12}$ , the room which one gram of matter † takes up in the æther is certainly less numerically than  $\pm 3.1 \times 10^{-17} \text{ c.c.}$ , probably less than  $\pm 10^{-17} \text{ c.c.}$ , and possibly nothing whatever.

25. Though the estimates just given rest on a conjectural value for the density of the æther, it may yet be of interest to express them in a different form. For matter other than hydrogen, the number of electrons in any atom is about half the atomic weight; and if we take  $10^{-13} \text{ cm.}$  as the radius of an electron, the total bulk of electrons in a gram of matter is roughly  $1.4 \times 10^{-15} \text{ c.c.}$  If  $\rho = 10^{12} \text{ grams per c.c.}$  (or any

\* Cf. Lodge, Phil. Mag. xiii. 1907; 'Nature,' lxxv. p. 519 (1907). The estimate is necessarily speculative; a revision of the argument in the light of more recent experimental data would, I think, tend to raise rather than to lower it.

† Strictly speaking, we are only entitled to state this of the iridio-platinum alloy used in the experiments.

higher value) the room (positive or negative) which 1 gram of matter takes up in the æther is certainly not more than  $1/45$  that of the total bulk of electrons, and is probably very much less.

The cost of the experimental work above referred to was partly defrayed by a Government grant received from the Royal Society.

Boars Hill, Oxford,  
Feb. 1914.

XCIV. *The Wave-Length of the Soft  $\gamma$  Rays from Radium B.*

By Sir ERNEST RUTHERFORD, *F.R.S.*, and E. N. DA C. ANDRADE, *B.Sc., Ph.D., John Harling Fellow, University of Manchester* \*.

[Plate XII.]

DURING the last few years, a large amount of attention has been directed to the absorption of the  $\gamma$  rays emitted by radioactive bodies. At first, the nature of the absorption by matter of the very penetrating  $\gamma$  rays emitted by the products radium C, mesothorium 2, thorium D, and uranium X, was carefully examined, and it was found that all these types of radiation were absorbed by light elements very nearly according to an exponential law over a large range of thickness, but with different constants of absorption for each radiation. In order to explain the emission of homogeneous groups of  $\beta$  rays from a number of products, Rutherford suggested that the  $\gamma$  rays emitted by the radioactive products must be regarded as the "characteristic" radiations excited in the radioelements by the escape of  $\beta$  particles from them. These "characteristic" radiations were supposed to be analogous to one or more of the groups of characteristic radiations observed by Barkla to be excited in different elements by X rays. It was suggested that the emission of homogeneous groups of  $\beta$  rays was directly connected with the emission of different types of characteristic  $\gamma$  rays from each element, and that the energy of the escaping  $\beta$  particle was diminished by multiples of definite units depending on the energy required to set the electronic system of the atom in a definite form of vibration.

In order to test this point of view, Rutherford and Richardson† analysed in detail the  $\gamma$  rays emitted by a

\* Communicated by the Authors.

† Rutherford and Richardson, *Phil. Mag.* May 1913, p. 722; August 1913, p. 325; Feb. 1914, p. 252.

number of radioactive substances, using the absorption method to distinguish broadly between the different types of  $\gamma$  rays emitted. It was found that the  $\gamma$  radiation from the B products, viz., radium B, thorium B, and actinium B, could all be conveniently divided into three types of widely different penetrating power. For example, the absorption coefficients in aluminium for the groups of  $\gamma$  rays from radium B were found to be 230, 40, and 0.5. In the case of the C products, viz., radium C, thorium C, and actinium C, the  $\gamma$  radiation was found to be mainly of one very penetrating type exponentially absorbed in aluminium. The radiations from the various radioactive substances can be conveniently divided into three distinct classes, viz. :— (1) a soft radiation, varying in different elements from  $\mu=24$  to  $\mu=45$ , probably corresponding to characteristic radiations of the “L” type excited in the radioatoms ; (2) a very penetrating radiation with a value of  $\mu$  in aluminium of about 0.1, probably corresponding to the “K” characteristic radiation of these heavy atoms ; (3) radiations of penetrating power intermediate between (1) and (2) corresponding to one or more types of characteristic radiations not so far observed with X rays.

In the meantime, the experiments of W. H. and W. L. Bragg\* and Moseley and Darwin† had shown that the reflexion of X rays from crystals afforded a definite and reliable method of studying the wave-length of X rays. It was found that the radiations from a platinum anticathode consisted in part of a series of strong lines, no doubt corresponding to the “L” characteristic radiation of this element. By using a number of anticathodes of different metals, the X-ray spectra of a number of elements were determined by W. H. and W. L. Bragg‡ and by Moseley§. The latter has made a comparative study of the strong lines of the spectra emitted by the great majority of the elements. For most of the lighter elements from aluminium to silver, the spectra obtained corresponded to the “K” characteristic radiations, while for the heavier elements the “L” series has been determined. The simple relations which Moseley finds to hold between the spectra of successive elements has been discussed by him in his recent paper.

\* W. H. Bragg and W. L. Bragg, Proc. Roy. Soc. A. lxxxviii. 1913, p. 428.

† H. G. J. Moseley and C. G. Darwin, Phil. Mag. July 1913, p. 210.

‡ W. H. Bragg and W. L. Bragg, Proc. Roy. Soc. A. lxxxix. 1913, p. 277, and *loc. cit.*

§ H. G. J. Moseley, Phil. Mag. Dec. 1913, p. 1024; April 1914, p. 705.



From the analysis of the types of  $\gamma$  rays, it appeared probable that each corresponded to one of the characteristic types of radiation of the element in question. It was consequently to be anticipated that each of these radiations would give definite line spectra when reflected from the surface of crystals.

In order to examine this question, experiments were begun to determine the wave-lengths of the  $\gamma$  radiations from the products radium B and radium C. For this purpose, a thin walled  $\alpha$ -ray tube, filled with a large quantity of emanation, served as a source of  $\gamma$  rays. The rays were allowed to fall at a definite angle on a crystal, generally rocksalt, and the intensities of the "reflected," or rather diffracted, rays were examined by a photographic method.

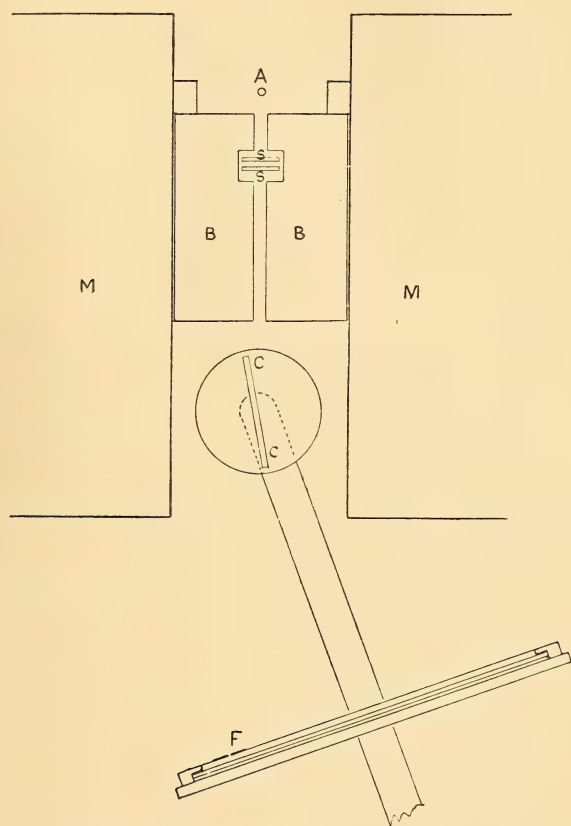
The determination of the  $\gamma$ -ray spectra is in some respects far more difficult than similar measurements for X rays. In the first place, the photographic effect of the  $\gamma$  rays, even from the strongest source of emanation available, is very feeble compared with that due to the X rays from an ordinary focus tube. For example, using a source of 100 millicuries of radium emanation, an exposure of 24 hours is necessary to obtain a marked photographic effect due to the reflected  $\gamma$  rays. Under similar conditions, 10 minutes exposure suffices to obtain a well-marked X-ray spectrum. In the second place, special precautions have to be taken to screen the photographic plate from the effects of the very penetrating  $\gamma$  radiation from radium C. The greatest difficulty of all, however, is to get rid of the disturbing effect of the very swift primary  $\beta$  particles emitted from the source and the swift  $\beta$  particles emitted from all material through which the  $\gamma$  rays pass. This can only be accomplished by placing the source of radiation, absorbing screens, and crystal in a strong magnetic field, so that practically all the  $\beta$  rays, both the primary ones and those excited by the  $\gamma$  rays in matter, are bent away from the photographic plate.

#### *Method of Experiment.*

The straight emanation tube, A, about 0.5 mm. in diameter and 1 cm. in length (fig. 1), was fixed behind a massive block of lead BB, so that the rays from it passed through a horizontal slit in the block; a square vertical hole in the lead allowed screens SS to be interposed in the path of the rays when desired. The length of the block from back to front was 6 cm., the width of the slit 3 mm. The emergent pencil of rays fell on the crystal CC, which was

mounted on a small turn-table so that the axis of revolution of the table passed accurately through the reflecting face; the angle of the crystal was measured on a metal scale by means of a glass pointer attached to the table. The emanation tube, lead block, and crystal were all placed between

Fig. 1.



the rectangular pole-pieces of a powerful electromagnet MM, as indicated in the diagram; the magnetic field usually employed was 2500 gauss.

The photographic plate was held with its film towards the source of the rays in a special carrier mounted on a rotating arm, the axis of rotation of which coincided with the axis of the crystal turn-table; in front of the film there was a single thickness of black paper to protect the plate from stray light. As it was possible that the position of the plate in the holder might vary in successive experiments, it was necessary for

purposes of measurement to mark its position relative to the holder. To enable this to be done, a narrow strip was removed from this black paper, and the hole thus formed covered with a slip of metal in which was a fine slit F; by means of a fixed lamp a fiducial line could then be marked on the plate, the plate-holder being always put in the same position for this purpose.

The distance of the source from the centre of the crystal was arranged so as to be exactly equal to the distance of this centre from the photographic plate (about 9 cm.). It is well known that under these conditions no correction for the length of the crystal is necessary in determining the angle of reflexion of the spectral lines, for reflexion of the same wave-length from any point of the crystal always falls at the same point on the plate. The crystal was arranged with the centre of its reflecting face as near as possible opposite the centre of the slit; the plate-holder was adjusted perpendicular to the slit for the zero reading. In making an experiment the crystal was set at a given angle with the central incident ray and the plate-holder rotated through double the angle from the zero position; the plate was inserted, the fiducial line marked on it, and an exposure of some hours (usually 24) was made, the magnetic field remaining on throughout. The crystals used were rocksalt and heavy spar. The whole apparatus was in a dark room.

Owing to the finite angle of the beam of  $\gamma$  rays, and to the length of the crystal, for any given setting of the crystal there are rays striking it at all angles within a certain small range. To enlarge the range and thus obtain more lines on the plate for a single exposure, the crystal was in some cases slowly rotated during the experiment, as in the experiments of M. de Broglie\*. The rotation was effected by the following device. Supported by the water in a tall cylindrical vessel was a float, which subsided slowly, owing to the escape of the water, drop by drop, through a capillary tube of suitable size attached to an opening in the bottom of the vessel. The float as it sank rotated the crystal by means of a light horizontal arm, to one end of which it was fastened by means of a thread passing over a pulley; the other end was attached to the turn-table carrying the crystal. The moving end of the arm was carried without friction by means of wheels on a glass plate, and the motion attained was very uniform and could be adjusted by changing the length of the capillary tube. A rotation of one degree occupied from four to eight hours.

\* M. de Broglie, *Journal de Physique*, Feb. 1914, p. 101.

*Measurement of the Plates.*

The positions of the lines were measured as distances from the fiducial line, which fixes the position of the plate relative to the plate-holder. From this was calculated the angle which the ray corresponding to any line made with the normal to the plate; the angle which the plate-holder made with the zero position being known, the angle of reflexion of the given ray followed at once. To correct for possible errors in the fixing of the zero, the same line was photographed twice, the crystal being rotated between the two photographs to a symmetrical position on the other side of the zero, so as to throw the line in the one case to the right, in the other case to the left, of the undeflected beam. This enables the angle of reflexion to be fixed with considerable accuracy if the zero positions are only roughly determined.

*Experimental Results.*

In this paper an analysis will be given of the soft type of  $\gamma$  radiation from radium B. Evidence of lines corresponding to the more penetrating rays from radium B and the penetrating rays from radium C has been obtained on the photographs, and the spectra have been separated by the interposition of absorbing screens; lines have been found, due to radium C, with 6 mm. of lead between the radium tube and the crystal. The spectra due to the penetrating rays from radium B and radium C are faint compared with that of the soft radiation from radium B, and have not yet been fully investigated; an account of them is withheld for a future paper.

The stronger lines due to radium B appeared with great distinctness on the photographic plate, as will be seen from fig. 2 (Pl. XII.), which is reproduced from an actual photograph; they permit of accurate measurement. In the photograph B is the band made by the direct rays coming through the slit,  $\beta$  and  $\alpha$  are the two strong lines formed by the reflected rays, and F is the fiducial line. The fainter lines do not appear on all the plates; however, no line is given in the table which has not been measured on at least two plates. The main feature of the spectra of the radiation reflected from rocksalt is two strong lines at almost exactly  $10^\circ$  and  $12^\circ$  respectively; they are accompanied by a number of fainter lines at angles of from  $8^\circ$  to  $14^\circ$ . There is also a large group of faint lines between  $18^\circ$  and  $22^\circ$ , which do not permit of accurate measurement, and so are omitted in the table; some of these, at least, are probably repetitions of the measured lines in the second order.

Most of the photographs were taken with crystals of



rocksalt, the crystal in some cases being a slip less than a millimetre thick, in others a specimen about a centimetre thick; the results did not differ noticeably for the soft rays. To check the measurements of the angles of reflexion made with the rocksalt, photographs were also taken by reflexion from the cleavage (001) face of a crystal of heavy spar (barium sulphate). Since the scattering by an atom is proportional to its atomic weight, it was thought that the heavy spar might give spectral lines of more intensity than the rocksalt for the more penetrating rays. In order to compare the constants, or "grating space," of the two crystals, special experiments were made with them both with X rays by the photographic method developed by Moseley, who kindly designed for us an X-ray tube with a nickel anticathode. This was provided with a side tube and slit, and the rays escaped through a thin aluminium window; the tube emitted an intense beam of soft X rays consisting mainly of the characteristic radiation of nickel. The angle of reflexion for the two strong lines in the nickel rays was directly determined for both rocksalt and heavy spar; for the (100) plane of rocksalt the angles obtained agreed closely with those determined by Moseley. The angles of reflexion from the (001) plane of heavy spar were found to be  $12^{\circ} 5'$  and  $13^{\circ} 23'$  in the first order. The ratio for the corresponding angles for the two crystals was 1.278. This enables us to compare numerically the photographs taken with the two crystals by the  $\gamma$  rays.

The spectra obtained with heavy spar appeared to be less intense than with rocksalt for the soft rays, and did not show the harder rays with much greater clearness. The angle of reflexion for the two strong lines of the radium B radiation were found to be  $7^{\circ} 52'$  and  $9^{\circ} 28'$ . Multiplying by the factor 1.278 to express them in terms of rocksalt, these become  $10^{\circ} 3'$  and  $12^{\circ} 6'$ , agreeing closely with the values obtained directly with this crystal. This puts it beyond doubt that the lines given by rocksalt are true diffraction lines, and do not arise from irregularities in the crystal.

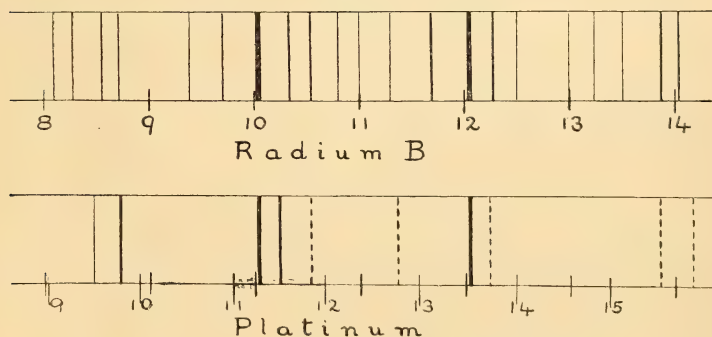
In the following table the angle of reflexion of the different homogeneous rays which make up the softer  $\gamma$  radiation from radium B are given for rocksalt. Their relative intensities are denoted by the letters "s." (strong), "m." (medium), and "f." (faint), but this indication is only very rough, as the circumstances conditioning the intensity vary from photograph to photograph. The wave-lengths (in centimetres) corresponding to the different angles of reflexion are calculated from the formula  $\lambda = 2d \sin \theta$ , the value

$d = 2.814 \times 10^{-8}$  cm. being taken from Moseley's paper. The spectrum of the characteristic radiation from platinum, suitably reduced by division by a constant factor, is added for comparison: this will be referred to again later (p. 864).

TABLE I.

RADIUM B. Soft $\gamma$ -ray spectrum.			PLATINUM. X-ray spectrum.
Angle of reflexion from rocksalt.	Wave-length (in cm.).	Intensity.	Angle of reflexion 1.122
8° 6'	$.793 \times 10^{-8}$	m.	
8° 16'	.809	m.	
8° 34'	.838	m.	8° 27'
8° 43'	.853	m.	8° 43'
9° 23'	.917	f.	
9° 45'	.953	m.	
10° 3'	.982	s.	10° 2'
10° 18'	1.006	m.	10° 13'
10° 32'	1.029	m.	
10° 48'	1.055	f.	
11° 0'	1.074	f.	
11° 17'	1.100	f.	
11° 42'	1.141	m.	
12° 3'	1.175	s.	12° 3'
12° 16'	1.196	m.	
12° 31'	1.219	f.	
13° 0'	1.266	f.	
13° 14'	1.286	f.	
13° 31'	1.315	f.	
13° 52'	1.349	m.	
14° 2'	1.365	m.	

Fig. 3.



In fig. 3 the spectrum is shown diagrammatically, and below it that of platinum, the scale being adjusted so as to

make the strong  $10^\circ$  line coincide with the corresponding platinum line. The dotted lines in the platinum spectrum are taken from a paper of de Broglie \*; as his determination of the strong line differs somewhat from that of Moseley and Darwin, the whole spectrum given by him has been reduced by multiplying by a constant factor chosen so as to make the strong lines agree.

### *Structure of the Spectral Lines.*

In the case of the stronger lines from rocksalt, viz. the  $10^\circ$  or  $12^\circ$  lines, the structure of the lines could be studied in some detail. They consisted of slightly curved bands about 0.5 mm. wide, the photographic intensity being greatest at the edge of the bands. A reproduction of part of one of these bands, magnified about five times, is shown in Pl. XII. fig. 4. With weak intensities only the outer edges of the band could be seen, and the band appeared as a close double. The spectral band appeared to be the exact mirror-image of the source, both as regards magnitude and distribution of intensity in radiation; the width of the image was the same as the diameter of the  $\alpha$ -ray tube, viz. 0.50 mm. The sharp and well-marked edges of the band are due to the fact that the intensity of the radiation is least from the centre of the cylindrical  $\alpha$ -ray tube, and increases to a maximum from the edges, owing to the active matter deposited on its inner surface. It is well known that a photograph taken of an  $\alpha$ -ray tube by its own rays through a narrow slit parallel to the source always shows these variations of intensity. The fact that the spectral band on the photographic plate is the mirror-image of the source, indicates clearly that the scattered rays forming the band come from very near the surface of the crystal. Attention has been drawn to the completeness of the reflexion of X rays from a crystal at the proper angle by Darwin †, and shown by him to be a necessary consequence of the mathematical theory. The efficiency of the reflexion is also well shown by recent experiments of W. L. Bragg ‡.

### *Imperfection of Crystals.*

In most of our experiments we have employed a crystal of rocksalt, since its structure has been worked out in detail by W. H. and W. L. Bragg, and since it gives fairly strong

\* *Journal de Physique*, loc. cit.

† C. G. Darwin, *Phil. Mag.* Feb. 1914, p. 315.

‡ W. L. Bragg, 'Nature,' March 1914, p. 31.

reflexions for soft radiations. The crystals employed, however, showed many imperfections, and their behaviour was very different from that to be expected for an ideal crystal; for example, when the crystal was set at an angle of  $12^\circ$  to the incident beam, and with the width of the pencil such that only radiations between  $11^\circ$  and  $13^\circ$  should be strongly reflected, in addition to the lines in this region other outside lines are observed in varying positions on the photographic plate: for example, in a particular case at  $2^\circ 40'$  and  $13^\circ 50'$ .

Special experiments showed that the position of these lines on the plate corresponded to a definite frequency of vibration in the incident beam. All our photographs showed similar peculiarities, but the outside lines which appear are very variable for different angles of the crystal. This behaviour of rocksalt led us to make many fruitless experiments to obtain a more perfect crystal, but all the crystals of rocksalt we have examined show similar imperfections, though in varying degrees. The crystal of heavy spar employed, for which the face appeared very plane and perfect, also behaved similarly. There appears to be no doubt that many crystals, and especially those of rocksalt, have a contorted or undulating surface, and that the orientation of the planes varies within certain limits from point to point of the crystal. At the same time, these irregularities may lead to the absence of a line in the photograph, although the crystal is set at the correct theoretical angle. To avoid this difficulty, it is desirable to keep the crystal in rotation during the experiment. Darwin has examined the consequences of such imperfections in a crystalline structure\*, and considers that they offer an explanation of the fact that the intensity of the reflected beam is in general greater than the theoretical value to be expected for an ideal crystal.

#### *Connexion of Radium B with Lead.*

In recent papers†, Moseley has examined the X-ray spectra of a number of the ordinary elements. For this purpose, each element either in the state of metal or compound is exposed as anticathode in a focus tube, and the resulting X-ray spectra are obtained photographically by the crystal method. He has shown that the "K" characteristic radiation of all the elements between aluminium and silver shows a similar type of spectrum, and the frequency of the corresponding lines changes by definite steps in passing from one

\* C. G. Darwin, *Phil. Mag.* April 1914, p. 975.

† *Phil. Mag. loc. cit.*



element to the next. The frequency of the strongest spectrum line has been shown to vary as  $(N-a)^2$  where  $N$  is a whole number and  $a$  a constant (about unity) for all this group of elements.  $N$  changes by unity in passing from one element to the next, and is supposed to represent the number of fundamental units of positive charge carried by the atomic nucleus and may for convenience be called the "atomic number," since it represents the number of the element when arranged in order of increasing atomic weight supposing that no elements are missing.

It is well known from the work of Barkla that the heavier atoms emit a second type of characteristic radiation known as the "L" radiation. Moseley has examined the X-ray spectra of this type for elements of atomic weight from silver to gold, and finds that the spectra of all these elements are similar, but as in the case of the "K" type, the frequency increases by definite steps as we pass from one element to the next. He has shown that the frequency of the chief line of the spectra is nearly proportional to  $(N-b)^2$ , where  $N$  as before is the atomic number (or nucleus charge) and  $b$  a constant (about 7.4) for the whole groups of elements.

On the general theory of the nucleus atom, the nucleus charge determines the chemical and physical properties of the atom, and it is consequently of great importance to determine the value of this constant for the radioactive atoms. Before the publication of this paper, Mr. Moseley kindly informed us of his experimental results, and it became of great interest to determine the nucleus charge of radium B. As we have already seen, the soft radiation from radium B, whose absorption coefficient is  $\mu=40$  in aluminium, was believed to be the "L" type of characteristic radiation of radium B, and this is completely borne out by the comparison of the  $\gamma$ -ray spectrum of the soft radiations of radium B with that of platinum (see page 861). Using Moseley's formula, and assuming for the atomic numbers the values to be given in a following paragraph, the factor by which the angle of the strong platinum line must be divided to give the angle of the corresponding line of radium B is 1.118: the value 1.122 used in Table I. was chosen so as to make the experimental lines agree exactly.

A determination of the nucleus charge of radium B is for another reason of the highest importance, for this radioactive element has been shown by Fleck to have the chemical properties of lead and to be chemically inseparable from it. As is well known, a very comprehensive and far reaching theory of the relation between the chemical and physical

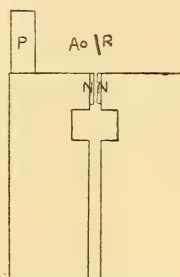
properties of the radioelements has been advanced by Fajans and Soddy. From the point of view of the nucleus theory of the atom, their conclusions may be expressed by the simple relation that the expulsion of an  $\alpha$  particle (carrying two positive charges) from an atom lowers its nucleus charge by two units, and the expulsion of a  $\beta$  particle (carrying one negative charge) raises its nucleus charge by one unit. Soddy has pointed out that the products radium B, actinium B, thorium B, and radium D are the "isotopes" of lead, *i. e.* they show identical chemical properties with those of lead, from which they are inseparable by chemical methods. If this view is correct, the atoms of these elements should have the same nucleus charge, although they may differ slightly in atomic weight.

If radium B has the same nucleus charge as lead, it must give an X-ray spectra almost identical with that of lead. It should, however, be pointed out that a very small variation in the frequency of the vibrations may be possible if the nuclear masses are different. In his recent paper (*loc. cit.*) Moseley has not determined the X-ray spectra of lead, but he kindly pointed out to us that on his results its atomic number or nucleus charge should be 82. He found gold had the nucleus charge 79; the two intervening elements, mercury and thallium, should have a nucleus charge of 80 and 81 respectively. From the relations found by him, it followed by calculation that the strongest line of lead should be reflected at  $12.07^\circ$  from rocksalt. The strongest line from radium B found by us was  $12.05^\circ$ —a very close agreement.

As it was possible, however, that there might be a small error in comparing the reflexion angles of rocksalt with different crystals and with such different experimental arrangements, it was decided to test by a straightforward method whether the X-ray spectra of radium B and lead were identical within the limits of experimental error. For this purpose it was arranged that the  $\gamma$ -ray spectra of radium B and of lead should be compared, using the same apparatus and under as nearly as possible identical conditions. H. Richardson, working in this laboratory, has found that the  $\beta$  rays expelled from radium B and radium C excite strongly the characteristic "L" type of radiation when they fall on heavy elements. In order to take advantage of this result, the  $\beta$  rays from an emanation tube of the kind already described were used to excite the characteristic radiation in a strip of lead, 1 mm. thick and 5 mm. broad, which was then used as the source in place of the tube itself, the rest of the apparatus being disposed much as before. The arrangement

was as shown in fig. 5 ; the slit was narrowed down to about 0.8 mm. by means of aluminium strips N, N, and the radiator R placed opposite it in the position indicated. The emanation tube A was fixed to one side, so that no direct rays

Fig. 5.



from it could strike the photographic plate. A second block of lead P was placed behind it, to increase the intensity by means of successive "reflexions" of the  $\beta$  rays between this block and R.

The spectrum of the radiation excited in the lead plate L was then determined under as nearly as possible the same conditions as for the  $\gamma$  rays from the emanation tube. For a given source, the photographic effect of the spectrum lines from lead only showed up faintly against the general blackening of the plate, but was sufficiently clear to admit of measurements of some of the angles of reflexion. Only a few lines of lead could be measured ; two of these gave reflexion angles of  $10^{\circ} 2'$  and  $12^{\circ} 0'$  in good agreement with the strong lines of the radium B spectrum. Other faint lines were also observed but were difficult to measure. There was, however, a possibility of error in such an experiment. It was conceivable that the spectrum lines observed were not due to the characteristic radiations from the lead but were to be ascribed to some of the soft  $\gamma$  radiations from radium B scattered by the lead plate. To test this point, the lead plate was replaced by one of platinum of the same dimensions and the spectrum again measured. The positions of the lines were quite distinct from those observed with the lead radiator, and the measurements of the reflexion angles of two of the strongest lines were in fair agreement with those given by Moseley and Darwin for platinum.

According to Moseley's results, the frequency of a reference line for the X-ray spectra of successive elements



changes by well-marked steps. For example, on the formula given by him, the reflexion angles from rocksalt of the strongest line of the spectrum from an element of nucleus charge 81 is  $12.41^\circ$ , for 82,  $12.07^\circ$ , for 83,  $11.77^\circ$ . In order to make a mistake of one unit in the nucleus charge, an error of 2 per cent. is necessary in measuring the angle of reflexion of the reference line, while the experimental determination of the reflexion angles of the  $\gamma$  rays from radium B is believed to be correct within 0.3 per cent.

It thus appears that the nucleus charge of radium B is the same as that of lead, for the atomic number of radium B, deduced by Moseley's formula from the  $\gamma$ -ray spectrum, is that to be expected for lead, and the strong lines of the  $\gamma$ -ray spectrum of radium B seem to be coincident with those of lead. According to radioactive calculation, the atomic weight of radium B is 214, while that of lead is 207. Provided the difference in atomic mass has not a large influence on the vibration frequencies of the outer distribution of electrons, it is to be anticipated that the ordinary light spectra of radium B and lead should be nearly identical, while we already know that these two elements have apparently identical chemical properties.

These results confirm in an unexpected way the correctness of this deduction of Soddy and Fajans, and also give a definite verification of the hypothesis that two elements of different atomic weights may have identical spectra and identical chemical properties. A similar result has been recorded by Sir J. J. Thomson and Aston in their work indicating that neon consists of a mixture of two gases of atomic weights about 20 and 22. The theory of the nucleus atom affords a simple explanation of such a result; for the chemical and physical properties are for the most part determined by the charge on the nucleus, and are practically independent of the mass of the nucleus. The properties of radioactivity and gravitation belong mainly to the nucleus. The fact that radium B is radioactive while lead is not, shows that the constitution of the nucleus is different in the two cases, and this is borne out by the known difference in atomic weights.

Taking the nucleus charge of radium B as 82, the nucleus charge of all the elements in the uranium-radium family can be deduced at once from the generalization already referred to. The numbers are given in the following table: an  $\alpha$  radiation gives a decrease of 2 in the nucleus charge, a  $\beta$  radiation an increase of 1.



TABLE II.

Element.	Radiation.	Atomic Number.
Uranium I. ....	$\alpha$	92
Uranium X <sub>1</sub> .....	$\beta$	90
Uranium X <sub>2</sub> .....	$\beta$	91
Uranium II.....	$\alpha$	92
Ionium .....	$\alpha$	90
Radium .....	$\alpha$	88
Emanation .....	$\alpha$	86
Radium A .....	$\alpha$	84
Radium B .....	$\beta$	82
Radium C .....	$\alpha + \beta$	83
Radium D .....	$\beta$	82
Radium E .....	$\beta$	83
Radium F .....	$\alpha$	84
End product (Lead)...	...	82

If the general formula of Moseley holds throughout, the frequencies of vibration of the "L" type of radiation for each of these elements can be simply calculated.

#### *Summary.*

(1) The  $\gamma$ -ray spectrum of the soft radiations from radium B has been examined by reflexion from the cleavage faces of crystals, and found to consist of a number of well-marked lines.

(2) The  $\gamma$ -ray spectrum of radium B is found to be of the same general type as that found for platinum and other heavy elements when bombarded by cathode rays.

(3) Attention is directed to the structure of the spectral lines using an emanation tube as source of radiation, and also to the imperfections of the crystals employed.

(4) Evidence is given indicating that the spectrum of the soft  $\gamma$ -rays spontaneously emitted from radium B, is identical within the limits of experimental error with the spectrum given by lead when the "L" characteristic radiation is excited by the bombardments of  $\beta$  rays.

(5) The bearing of these results on the structure of the atom is discussed.

XCV. *Regular Surface Markings in Stretched Wires of Soft Metals.* By E. N. DA C. ANDRADE, B.Sc., Ph.D., late 1851 Exhibition Scholar of University College, London\*.

[Plate XIII.]

IN a study of the flow in metals, an account of which is now in course of publication, experiments were made with wires of solid mercury. These were prepared by filling with mercury a mould composed of two hollow glass hooks connected to each end of a thin glass tube by rubber junctions, and then immersing the whole in a bath of solid carbon dioxide and alcohol; when the mercury was frozen solid the glass tube, previously scored with a diamond, was quickly broken off, leaving a wire of solid mercury fastened into a glass hook at each end. For the experiments in question such wires, maintained at a temperature of  $-78^{\circ}\text{C.}$ , were extended until they broke; it was then observed that the fracture, instead of showing a contraction to a symmetrical point, as is usual with other metals, had a flattened form, contraction having taken place in one azimuth only. This may be referred to as a chisel-edge fracture. Soon after I had made this observation Mr. B. B. Baker, working in the same laboratory, informed me that he had noticed a similar phenomenon in some sodium wires on which he was experimenting, accompanied by semicircular markings of great regularity†. I therefore examined the mercury wires for these markings, and was able to observe them easily with a lens magnifying a few times. A photograph of a portion of a mercury wire showing the markings, magnified about five times, is given in Pl. XIII. fig. 1. I had previously observed that both tin and lead wires (a very pure specimen) showed marked roughenings of the previously smooth surface of the wire on extension; the markings seemed to have some regularity. After carefully annealing the lead and tin wires at temperatures near their respective melting-points for some hours I obtained, on stretching the wires, the semicircular markings with great distinctness for tin (fig. 2), and fairly well marked for lead (fig. 3). The photographs for the lead and tin were taken with a magnification of ten times: that of the lead shows the broken end of the wire. Fig. 4 shows the markings for tin magnified about 130 times.

The wires exhibiting the markings show the one-sided contraction not only at the fracture, but throughout the

\* Communicated by Prof. A. W. Porter, F.R.S.

† See B. B. Baker, Proceedings of the London Physical Society, 1913. *Phil. Mag.* S. 6. Vol. 27. No. 161, May 1914. 3 M

length. That is, they contract in a particular azimuth only, retaining in the azimuth normal to this the diameter of the unstretched wire. The cross section of a wire behaving in this way appears to be roughly elliptical, so the contraction is approximately uniform across the wire. The minor axis of such a cross section is, in the case of tin, often only 0.4 of the major. The ring-shaped markings appear on the flatter surfaces of the wires, which are shown in the photographs; they are similar on each flattened side and run together at a sharp angle at the edges of the flattened wire. The plane in which the flattening takes place must be determined by chance asymmetrical irregularities, for with tin two or more such different planes sometimes occur on the same wire, separated by small lengths in which the wire retains its original circular form, and shows no regular markings.

Thus on extending wires of the soft pure metals mercury, tin, and lead (and also sodium and potassium, as shown by Baker), we are able to get surface markings of great regularity, accompanied by a contraction of the wire in one particular direction only. The markings present the appearance of a series of equal layers which have been sheared over one another, as would be the case with a half cylinder composed of semicircular plates if the plates were all tilted over to make an acute angle with the axis of the cylinder. They are probably due to large uniform crystals, of a size comparable with the diameter of the wire, arranged in layers, which behave somewhat in the way suggested. It is noticeable that the metals which give the phenomenon are all very soft, a condition to which large crystals are known to be favourable. The purer lead which shows the markings is softer than ordinary commercial lead. The phenomenon has evidently nothing to do with the processes to which the wire is subjected during manufacture, as the specimens of lead and tin have to be thoroughly annealed if they are to show it well.

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XCVI. *Thermodynamics of Radiation.* By H. L. CALLENDAR, M.A., LL.D., F.R.S., *Professor of Physics at the Imperial College, S.W.\**

IN the number of this Journal for October 1913, p. 787, I gave a brief sketch of a theory of radiation and specific heat, which appeared to be worth recording on account of its simplicity and its good agreement with experiment. The formula given for the distribution of energy in full radiation

\* Communicated by the Author.

was deduced, in the first instance, from a quasi-molecular theory of radiation, and free use was made of the close analogy between full radiation and an ideal vapour, as being the method most likely to appeal to experimentalists familiar with the application of the gas analogy to other branches of physics. The same result might have been deduced in a variety of other ways, since it is to a great extent independent of the particular analogy employed. It now seems desirable to give an alternative method, which has the advantage of being more direct and of throwing more light on the essential points of difference between the proposed theory and that commonly accepted.

In order to explain the notation and to indicate the assumptions which are taken as the basis of the present method, it will be well to give a brief summary of the fundamental facts, which are generally accepted, and are to be found in many textbooks, such as Poynting's 'Heat,' cap. xx. p. 333.

*The Energy Stream Q.*—A study of the laws of emission and absorption of radiation in relation to the equilibrium of temperature, has led to the conclusion that the condition existing inside a vacuum enclosure at a uniform temperature  $T$  may be represented by an isotropic energy-stream  $Q$  per second per sq. cm., which is the same in every direction and in all parts of the enclosure, and is a function solely of the temperature. A similar proposition must be true for each separate frequency into which the radiation may be analysed. We may define  $q$  as the energy-stream of a particular frequency  $\nu$  per unit range of frequency, such that  $q d\nu$  represents the energy-stream included between the limits of frequency  $\nu$  and  $\nu + d\nu$  in full radiation. The partial stream  $q$  is a function only of the temperature  $T$  in addition to the frequency considered. Its rate of variation with temperature  $(dq/dT)_\nu$  at constant frequency is equally definite.

*The Energy Density U.*—If we suppose the radiation to be continually travelling in all directions with the velocity of light  $c$ , the energy-density of the stream  $Q$ , or the quantity existing in the medium at any moment per c. c., will be  $4Q/c$ , for the full stream  $Q$ . Similarly the energy-density  $u$  per unit range of frequency will be  $4q/c$ , for the partial stream  $q$ .

*The Doppler Effect.*—The simplest case to consider is that of a perfectly reflecting sphere expanding symmetrically with uniform velocity, small compared with that of light, and filled with a homogeneous and isotropic mixture of different frequencies. As the sphere expands, the wave-length of



every component in the mixture will increase in direct proportion to the radius of the sphere, whatever the angle of incidence. Each component may be regarded as retaining its identity while its frequency varies, and any arbitrary distribution of components will be permanent as regards the ratio of the energies of the different components\*.

*Law of Adiabatic Expansion.*—The simplest assumption to make with regard to the variation of energy is that, when a given quantity of radiation is adiabatically compressed or expanded in a perfect reflector, the whole energy of each component which retains its identity varies directly as its frequency. This assumption is in agreement with electromagnetic theory, and is equivalent to various other assumptions which have been made for the deduction of the pressure. The energy stream  $qdv$  of the component included between limits  $\nu$  and  $\nu + d\nu$  of frequency in an expanding sphere of radius  $r$ , is transformed into a stream  $q'd\nu'$  when the radius has increased to  $r'$ , and is included in an interval  $d\nu'/\nu'$  which is equal to  $d\nu/\nu$ , where  $\nu'/\nu = r/r'$  in virtue of the Doppler effect. The whole energy of the component  $qdv$  at any stage is the product of the volume  $4\pi r^3/3$  and the energy-density  $4qdv/c$ . By the above assumption the whole energy varies as  $1/r$ , so that  $r^4qdv$  is constant. The energy-stream  $qdv$  of each component varies directly as the fourth power of its frequency  $\nu$ , or inversely as the fourth power of the radius  $r$ .

*The Radiation Pressure.*—The pressure  $p dv$  due to the stream  $qdv$  is directly deducible by equating the work done  $p dv \times 4\pi r^2 dr$  in a small expansion  $dr$  to the loss of energy of the stream. The expression for the whole energy of the stream may be written  $(r^4 qdv) 16\pi/3rc$ . Since  $r^4 qdv$  is constant, the loss of energy in a small expansion  $dr$  is  $(r^4 qdv) 16dr/3r^2c$ . Equating this to the work we obtain  $p = 4q/3c$ , which is true for each component separately; and similarly  $P = 4Q/3c$  for the whole radiation. It will be observed that the pressure and the work result essentially from change of frequency caused by the Doppler effect.

*The Temperature of Full Radiation.*—It is shown in many textbooks (*e. g.* Poynting, p. 337) that "full radiation remains full radiation in any adiabatic change." It follows by a direct application of Carnot's cycle to full radiation, that the temperature  $T$ , as defined by Carnot's principle, varies directly as the frequency of each component, or inversely as the radius of the expanding sphere. The energy-density and the pressure vary as the fourth power of the temperature for the radiation as a whole (the Stefan-Boltzmann

\* Larmor, Brit. Assoc. Rep. 1900, p. 657.

law), and also for each component considered separately. The product  $\lambda T$ , or the ratio  $\nu/T$ , remains constant for each component, which is Wien's displacement law. Both laws are summed up in Wien's general expression for the distribution in full radiation, which gives for  $q$  as already defined,

$$q = C\nu^3 F(\nu/T) = CT^3 f(\nu/T), \quad . . . . (1)$$

where  $F$  and  $f$  are undetermined functions expressing the distribution in full radiation.

### *Extensions of the Theory.*

So far we have been considering only those theoretical relations which result from the Doppler effect on components of variable frequency which retain their identity in adiabatic expansion. These relations have been verified indirectly, and are universally admitted. The extensions which I have proposed result from a consideration of *isothermal emission* at constant frequency. In experimental work it is impossible to isolate and trace the components of variable frequency ( $\nu/T$  constant), or to perform an adiabatic expansion. We have to deal with rays of constant frequency, separated and measured under the condition of steady flow at constant temperature.

The main points which I have endeavoured to establish are the following:—

(1) Since, so far as we know, each frequency is propagated without change in free space, the heat taken from the source by the emission of a steady stream of a particular frequency should, by the first law of thermodynamics, be equal to the heat evolved on condensation of the same stream in the receiver. Although it is not possible to trace all the steps of an irreversible process, such as radiation from a higher to a lower temperature, the change of total heat must be the same as that calculated by a reversible path. The first requisite, therefore, is to find the latent heat of isothermal emission of a particular frequency.

(2) It has always been tacitly assumed that the energy-density of each frequency in an isothermal enclosure is directly proportional to the heat measured on absorption, which is equivalent to assuming the latent heat of emission per unit volume proportional to the energy-stream  $q$ . I have maintained on the contrary, in the paper already quoted, that the latent heat of emission per unit volume for each frequency should be that given by Carnot's principle, namely  $T(dp/dT)_\nu$ ,

which is proportional to  $T(dq/dT)_\nu$ , but is not proportional to  $q$ . It may be objected, with apparent reason, that Carnot's principle cannot be applied to each particular frequency in isothermal emission under equilibrium conditions on account of the change of frequency caused by the Doppler effect at the moving piston or expanding wall of the enclosure. It is therefore necessary to show that the expression  $T(dp/dT)_\nu$  for the latent heat given by Carnot's principle, is not in conflict with the Doppler effect in adiabatic expansion, but follows directly from it.

*Latent Heat  $l$  of Isothermal Emission of a Particular Frequency.*—Taking the perfectly reflecting sphere already considered, and supposed full of radiation in equilibrium at a temperature  $T$ , let the radius of the sphere expand by a small increment  $dr$ , so that the enclosed radiation falls to a lower temperature  $T-dT$ , where  $-dT = Tdr/r$  as already explained. The stream of energy  $q$  per unit range of a particular frequency  $\nu$  at the original temperature  $T$  will be reduced at the lower temperature  $T-dT$  to the value  $q - (dq/dT)_\nu dT$ , where  $(dq/dT)_\nu$  is the rate of change of  $q$  with temperature for a *constant* frequency, which has a perfectly definite value for each frequency in full radiation. If now the perfectly reflecting surface is replaced by an emitting surface at the original temperature  $T$ , equilibrium will be restored by the absorption of the existing stream  $q - (dq/dT)_\nu dT$  and the emission of a stream  $q$  at constant volume. The volume, which remains constant during this process, may be taken as  $4\pi r^3/3$ . The final energy-density is  $4q/c$ . The *net* energy emitted will therefore be  $16\pi r^3(dq/dT)_\nu dT/3c$ , which reduces to  $16\pi r^2 T(dq/dT)_\nu dr/3c$ , by substituting for  $dT$  its value given above. The latent heat of emission  $l$  *per unit increase of volume* is obtained by dividing this by the increase of volume, namely,  $4\pi r^2 dr$ , which gives  $l = 4T(dq/dT)_\nu/3c$ , or  $T(dp/dT)_\nu$ , since  $p = 4q/3c$ .

The above method may appear at first sight to be unnecessarily circuitous, but it is really the most direct for deducing the required result from the *admitted* properties of the energy-stream and the Doppler effect in adiabatic expansion. The same procedure is applied in the reverse direction in elementary thermodynamics in deducing the fall of temperature  $dT$  for a small adiabatic expansion  $dv$  in the case of a perfect gas, by equating the heat,  $sdT$ , required to raise the temperature at constant volume, to the work done  $p dv$ , or the heat absorbed  $RT dv/v$ , in the same expansion performed under isothermal conditions.

Admitting the existence of the Doppler effect in isothermal



emission under equilibrium conditions at the slowly expanding wall of the enclosure, it is easy to see why the latent heat of a particular frequency per unit volume should be different from the density of the energy-stream of the same frequency together with the external work. The higher frequencies are being continually degraded into lower during the motion, so that the actual net amount of a high frequency emitted may be greatly in excess of the quantity  $4p$  per unit volume which would be required if there were no degradation of frequency. On the other hand, for a low frequency, the amount required to maintain the energy-stream at its equilibrium value is greatly reduced by the return of energy degraded from the higher frequencies. The two effects balance in the case of full radiation at the mean point where  $T(dp/dT)_v = 4p$ .

The nature of the effect considered may also be illustrated by a consideration of the relation between the partial differential coefficients. If  $(dp/dT)_x$  represents the rate of change of  $p$  with  $T$  in adiabatic expansion when  $\lambda T$  or  $\nu/T$  is constant, we have the general relations, representing Wien's displacement law (1),

$$T(dp/dT)_x = 3p = \nu(dp/d\nu)_x = T(dp/dT)_v + \nu(dp/d\nu)_T. \quad (2)$$

Similar relations hold for  $q$  and  $u$ , which are simply proportional to  $p$ . The latent heat  $T(dp/dT)_v$  is not equal to  $4p$ , but to  $3p - \nu(dp/d\nu)_T$ . The coefficient  $(dp/d\nu)_T$  is obviously positive on the low frequency side of the curve representing  $p$  plotted against  $\nu$  at constant temperature, where the latent heat is less than  $3p$ . It vanishes at the maximum of the pressure curve, where  $T(dp/dT)_v = 3p$ , but it may attain large negative values for high frequencies.

*The Entropy, and Intrinsic Energy.*—If the latent heat is represented by  $T(dp/dT)_v$  per unit range and volume, the entropy should be simply  $(dp/dT)_v$ . The *internal latent heat* per unit volume,  $T(dp/dT)_v - p$ , or the intrinsic energy denoted by  $E/\nu$  in the previous paper, is the energy carried by the stream of a particular frequency, and given up on condensation in addition to the work  $p$ . It follows from Wien's displacement law (1) that the ratio,  $E/p\nu$ , of the intrinsic energy to the pressure, *must* be some function of  $(\nu/T)$ , depending on the distribution. It was assumed in the previous paper that  $E/p\nu$  for full radiation was of the form  $b\nu/T$  (where  $b$  is a constant required by the arbitrary nature of the units) on the ground that the intrinsic energy of a given quantity varies as the frequency. This assumption fixes the distribution in full radiation, and leads to the



simplest relations between the various quantities, in addition to giving very good agreement with experiment. The intrinsic energy of a volume  $v$  such that  $pv=RT$ , is simply  $Rbv$ , and the corresponding expression for the entropy is  $R(1+bv/T)$ .

If the latent heat equation,  $T(dp/dT)_v = E/v + p$ , is integrated at constant frequency on the assumption  $E/pv = bv/T$ , we obtain immediately the expressions previously given (*loc. cit.*) for the partial pressure, intrinsic energy, and latent heat, per unit range of  $\nu$ , namely,

$$\text{Partial Pressure, } pd\nu = C\nu^2 Te^{-bv/T} d\nu, \quad . \quad . \quad . \quad (4)$$

$$\text{Intrinsic Energy, } (E/v)d\nu = Cbv^3 e^{-bv/T} d\nu, \quad . \quad . \quad (5)$$

$$\text{Latent Heat, } ld\nu = C\nu^2 T(1 + bv/T)e^{-bv/T} d\nu, \quad (6)$$

The partial pressure  $p$  is proportional to the energy-stream  $q$  in an isothermal enclosure, and is identical in form with the expression originally proposed by Lord Rayleigh (*Phil. Mag.* xlix. p. 539, 1900) to represent the energy-stream. His method was founded on the doctrine of the equipartition of energy, and gave no explanation of the exponential term. This factor arises in the present investigation directly from Carnot's principle, and is explained by the continual degradation of the higher frequencies owing to the Doppler effect in isothermal emission, which appears to afford a possible way out of the difficulty raised by Jeans in discussing the problem from the point of view of equipartition.

#### *Comparison with Experiment.*

The quantity measured in experimental work is either the rate of loss of heat of a more or less perfect radiator, or else the rate of reception of heat by a receiver absorbing a known fraction of the radiation from a source of the "black body" type. In either case the quantity measured is proportional to the latent heat of emission as already defined, and not to the energy-stream existing in the state of equilibrium, except in the case of full radiation for which  $T(dQ/dT) = 4Q$ . The full stream,  $Q = \sigma T^4$ , emitted per second per sq. cm. from a small aperture in a black body at a uniform temperature  $T$ , is equal to  $c/4$  of the full energy density  $U$ , or to  $3c/4$  of the full pressure  $P$ , and is the same as  $T(dQ/dT)/4$ . But the quantity measured for each separate frequency per unit range is *not*  $q = \dot{c}u/4 = 3cp/4$ , as generally assumed, but  $T(dq/dT)_\nu/4$ , which is proportional to the latent heat of emission  $T(dp/dT)_\nu$  per unit volume. The value of the full pressure  $P$ , obtained

by integrating the partial pressure  $p dv$  from 0 to infinity at constant  $T$ , is

$$P = 2CT^4/b^3 = 4Q/3c = 4\sigma T^4/3c. \quad (7)$$

Whence the value of the constant  $C$  is  $2\sigma b^3/3c$ . Substituting this value of the constant  $C$  in the equation for the latent heat  $ldv$  per unit volume, we obtain the equation for the latent heat of emission per second, per sq. cm., in terms of the radiation constant  $\sigma$ ,

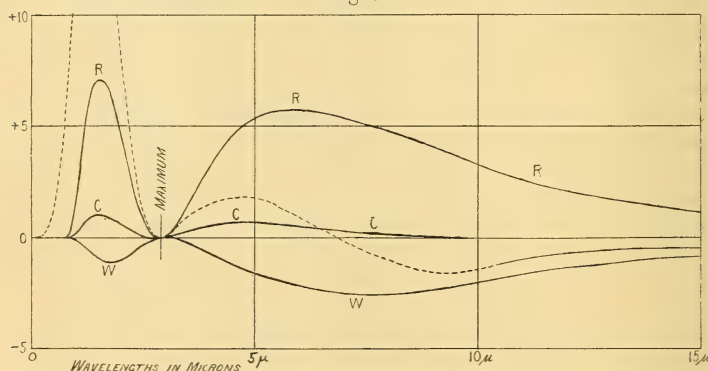
$$2T(dq/dT)_{\nu} dv = \sigma b^3 \nu^2 T(1 + b\nu/T)e^{-b\nu/T} d\nu, \quad (8)$$

which represents the curve of distribution of energy, as experimentally observed, plotted against the frequency as abscissa. The corresponding curve with the wave-length  $\lambda$  as abscissa is obtained by substituting  $\nu = c/\lambda$ , and  $d\nu = -cd\lambda/\lambda^2$ . The curve plotted in terms of wave-length has a maximum at the point where  $\lambda T = (\sqrt{2} - 1)bc/2 = \cdot 2071bc$ . The mean of various experimental determinations puts the maximum of the wave-length curve at  $\lambda T = \cdot 290$ , when the wave-length is measured in cms. Whence the value of the constant  $bc = 1\cdot 400$ . The curve obtained with this value of the constant  $bc$  gives very good agreement with experiment, both for the distribution curve at constant temperature, and for the variation with temperature of the energy of a particular frequency, both of which are included in the same formula (8) by putting either  $T$  or  $\nu$  constant,

It is at once evident that a formula of the type shown in (8) must be capable of representing the distribution curve with considerable accuracy, since it reduces to the same type as Wien's when  $\lambda T$  is small or  $b\nu/T$  large, and to the same type as Rayleigh's when  $\lambda T$  is large or  $b\nu/T$  small. It would be tedious and unnecessary to analyse all the observations (though this has been done) since it is generally admitted that Planck's formula fairly represents the experimental data. It may be of interest, however, to give curves showing the differences between the formulæ, if only to illustrate the limitations of experimental verification. The formulæ compared are those of Wien, Planck, Rayleigh, Walker and Callendar. The value of the distribution constant  $b$  is calculated for each formula from the position of the maximum by taking the same value of  $\lambda_m T$ , namely,  $\cdot 290$ , for all. If the same absolute value of the Stefan constant  $\sigma$  were also taken for all, the absolute value of the maximum would be different for each formula. But since only relative values are obtainable experimentally in the distribution curve, the maximum for each formula has been reduced to 100, and the

differences from Planck's formula (represented by the base line), expressed as a percentage of the maximum, are plotted in the curves. The differences are plotted on a wave-length base for a temperature  $T=1000^{\circ}$  Abs., for which the maximum occurs at the point  $\lambda=2.9\mu$  where all the formulæ are made to agree. It is well known that the formulæ of Wien and Rayleigh (R) differ appreciably from experiment, but it is remarkable how closely the sum of the two, represented by curve (C), agrees with Planck's expression  $q_{\lambda}d\lambda=k\lambda^{-5}(e^{hc/\lambda T}-1)^{-1}$ . The maximum difference of 1 per cent, which occurs on the short wave-length side of the maximum, would be difficult to verify in the distribution curve owing to its steepness on this side, and might be compensated by a very slight shift of the maximum. There are, however, several observations which indicate that Planck's formula gives results a little too low for short wave-lengths.

Fig. 1.



Differences of Distribution Formulæ from Planck's Formula at  $1000^{\circ}$  Abs. on wave-length base, expressed in per cent. of maximum.  
R, Rayleigh; C, Callendar; W, Wien; dotted, Walker.

On the short wave-length side, an interesting contrast is presented by the ingenious empirical formula recently proposed by G. W. Walker (Proc. R. S. A lxxxix. p. 393, 1914) on dynamical grounds, as representing the harmonic analysis of an arbitrary series of disturbances with strictly aperiodic damping. Walker's formula is a modification of that of Kövesligethy, 1890, and is of the type,

$$E_{\lambda}=kT^5[\lambda T/(\lambda^2T^2+a^2)]^4, \dots (9)$$

which evidently satisfies the conditions laid down by Wien, but does not otherwise conform to the present theory. The curve as shown by Walker is very similar in general appearance to the distribution curves of Lummer and Pringsheim, especially



on the side of long wave-lengths, where the comparison is fairly easy. But if the *differences* are plotted as in figure (1) (dotted curve), they amount, on the short wave-length side, to something of the order of 20 per cent. of the maximum ordinate, which considerably exceeds the possible limits of error of the verification of Wien's or Planck's formulæ in this region. According to Walker's formula the thermal intensity of the ultra-violet light of wave-length  $29\mu$  in the radiation from a black body at  $727^\circ\text{C}$ . (a dull red heat) should be  $\cdot 154$  per cent. of the maximum ordinate, and might be detected with a sensitive thermopile. As a matter of experiment no radiation of this wave-length from such a source can be detected by the most delicate photographic methods, and it is much more likely to be of the order of  $10^{-15}$  of the maximum, as given by Wien's formula. The exponential rate of diminution of the curve on the short wave-length side is one of the most certain results of experiment, and it is one of the strongest points of the present theory that the exponential term in the formula follows so directly from the application of Carnot's principle.

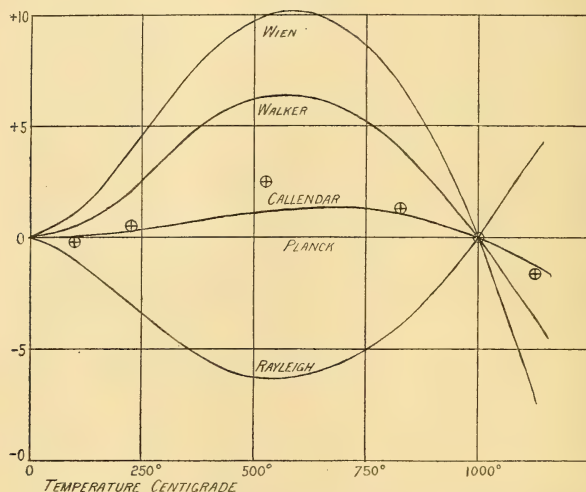
Another method of comparing the formulæ with experiment is to observe the variation with temperature of the intensity of a particular wave-length. Among the best known applications of this method are the experiments of Rubens on the *Reststrahlen* of quartz, fluorite, and rocksalt. His experiments showed clearly that the distribution formula must reduce to the Rayleigh type  $k\lambda^{-4}T$  for large values of  $\lambda T$ , but indicated appreciable deviations from Planck's formula in the case of the quartz *Reststrahlen*. The *difference* between his results and Planck's formula is shown by the crosses representing the observations in fig. 2. Planck's formula itself is represented by the base-line as in the previous figure.

Here again, as Rubens points out, comparison of the relative values alone is experimentally possible. The values given by the various formulæ for radiation of wave-length  $8\cdot 85\mu$ , corresponding to the quartz *Reststrahlen*, with the source at  $1000^\circ\text{C}$ . and the receiver at  $0^\circ\text{C}$ ., are accordingly reduced to a common value, so that all the curves agree at  $0^\circ\text{C}$ . and  $1000^\circ\text{C}$ ., and the differences from Planck's formula at intermediate points are plotted in terms of the radiation at  $1000^\circ\text{C}$ . The observations are seen to agree distinctly better with the thermodynamical formula (8) than with Planck's. The observations on the *Reststrahlen* of fluorite and rocksalt show a similar result, but are not so decisive, because the formulæ approximate so closely to the Rayleigh type for long wave-lengths, and the observations are



less concordant on account of the feebleness of the radiation to be measured, which is about 200 times less for rocksalt than for quartz at  $1000^{\circ}\text{C}$ .

Fig. 2.



Difference of Rubens' Observations on Quartz Reststrahlen from Planck's formula, compared with other formulæ.

The agreement of the proposed formula (8) with direct experiments on radiation is seen to be satisfactory. As indicated in the previous paper, the agreement with atomic theory as regards (1) the number of atoms  $N = 6.12 \times 10^{23}$  in a gramme atom, and (2) the atomic unit of energy per unit frequency  $Rb/N = 6.34 \times 10^{-27}$ , is equally satisfactory, according to the estimates of these quantities obtained from other sources. The variation of specific heat at low temperatures can also be represented by the thermodynamical formula with fewer arbitrary hypotheses than by Planck's. These, however, are questions involving many speculative elements, and are of little weight compared with the thermodynamical argument on which the formula is founded. The Doppler effect must occur in the isothermal emission of an energy-stream, and has not been considered in this connexion. That it should lead directly to Carnot's expression  $T(dp/dT)_v$  for the latent heat per unit volume, is too striking a confirmation of the principles of the classical thermodynamics to be disregarded. According to my view, it affords an additional relation, which suffices, in conjunction with Wien's law, to fix the distribution in full radiation.

XCVII. *The Intensity of Reflexion of X Rays by Crystals.*  
 By W. H. BRAGG, M.A., F.R.S., *Cavendish Professor*  
*of Physics in the University of Leeds* \*.

WHEN a pencil of homogeneous X rays is incident upon a crystal face it is reflected when, and only when, the angle  $\theta$  between the pencil and the face satisfies the equation

$$n\lambda = 2d \sin \theta \dagger,$$

where  $\lambda$  is the wave-length of the rays,  $n$  is an integer, and  $d$  is the distance between any plane and the nearest which is similar and similarly placed. In the simplest kind of arrangement, all the planes are similar and equally spaced, and  $d$  is then the distance between two neighbouring planes.

If  $\lambda$  and  $d$  are given, if, that is to say, a certain X-ray pencil falls on a certain crystal face, several values of  $\theta$  may be found to satisfy the equation, corresponding to consecutive values of the integer. The reflexions occurring at the angles

$$\sin^{-1} \frac{\lambda}{2d}, \quad \sin^{-1} \frac{2\lambda}{2d}, \quad \sin^{-1} \frac{3\lambda}{2d}, \quad \dots$$

may be called the reflexions or spectra of the first, second, third order, and so on.

When the planes are equal and equally spaced the intensities of the reflexions decrease rapidly and continuously as  $n$  increases; reflexions of an order higher than the fifth or perhaps the sixth have not been observed.

When the arrangement of planes is more complicated this regular diminution in intensity may be greatly modified. Complication may arise in either or both of two ways. The planes may be unequally spaced, or they may be dissimilar. An example of the former effect is to be found in the reflexion from the cleavage face (111) of the diamond. In this case the planes are arranged at distances apart which are alternately as 1 to 3 ‡. In consequence the second order reflexion disappears entirely (*loc. cit.*). The intensity of the third and fifth are normal in comparison with the first, but the fourth is twice as strong as it should be.

An example of the effect of want of similarity in the planes may be illustrated by reference to the (111) planes of rock-salt §. In this case the spacing is uniform but the planes

\* Communicated by the Author.

† W. L. Bragg, *Proc. Camb. Phil. Soc.* xvii. p. 43.

‡ W. H. Bragg and W. L. Bragg, *Proc. Roy. Soc.* lxxxix. p. 277.

§ W. L. Bragg, *Proc. Roy. Soc.* lxxxix. p. 274.

contain alternately sodium atoms only and chlorine atoms only. The result of this unequal loading is that the reflexions of even order are strongly enhanced in comparison with those of odd order: we are taking  $d$  to be the distance from one chlorine plane to the next, in accordance with the definition given above, and the glancing angle of the first order to be  $\sin^{-1}\lambda/2d$ .

When both spacings and loadings are irregular the relative intensities are more complicated still; as for example in the case of reflexion by the (100) or (111) planes of iron pyrites\*.

Since the relative intensities depend so directly upon the spacings and loadings of the planes, and since the manner of dependence can be easily explained, it follows that experimental determinations of the intensities may be used to draw conclusions as to the structure of the crystal in question. This method has been largely used by W. Lawrence Bragg†.

It is of importance, therefore, that the intensities should be measured with as much accuracy as is possible. It happens that this method of analysis is extraordinarily powerful, and that very rough measurements coupled with general assumptions have been sufficient to lead, in the paper quoted, to definite conclusions. The measurements which were used, and for which I was myself mainly responsible, could only be considered as provisional, under the circumstances. They were sufficient, however, for the determination of several complicated crystals, such as iron pyrites, the calcite series, and so on.

For example, in the case of iron pyrites it appeared that the iron atoms were arranged on a face-centred cube, that is to say, at the corners of a cube and at the centres of each face. A sulphur atom lay in each of the eight small cubes into which the large cube could be divided; it was situated on a diagonal of the small cube which diagonal was to be chosen in a special way, and calculation determined the position as dividing the diagonal in the ratio 1:4. Ewald has now shown (*Phys. Zeit.* April 15, 1914) that by the aid of this determination of the structure of iron pyrites, the Laue photographs of the crystal can be completely unravelled, and the structure is therefore confirmed by an independent method. One small change is all that is required. In order to explain the relative intensities of certain of the less prominent spots in the photograph, it is

\* W. L. Bragg, *Proc. Roy. Soc.* lxxxix. p. 476.

† *Proc. Roy. Soc.* lxxxix. p. 468.

necessary to suppose that the sulphur atom divides the diagonal, not in the ratio 0.2 to 0.8, as W. L. Bragg had found, but more nearly as 0.224 to 0.776.

If, therefore, it has been possible to find so much from the early and rough measurements of intensity, it ought to be possible to do far more if the measurements are made more accurate.

There are other reasons for attempting to increase the accuracy of the intensity determinations. In the first place, it will be possible in this way to test theories which profess to explain the general process of reflexion of X rays by crystals. And again, it is important to be able to determine to what extent the intensities are dependent on the temperature of the crystal. The thermal movements of the atoms should affect the reflexion; indeed, Debye has calculated the extent to which they should do so\*. Experiment should therefore be of great use in this direction also.

For these various reasons I have endeavoured to increase the degree of accuracy with which intensities can be compared by means of the spectrometer. This paper contains a brief account of the method which appears to be the most suitable, and gives some results of its application to rock-salt and to the diamond. Although much greater accuracy is no doubt still obtainable, the determinations already made seem capable of being applied usefully.

Let us first attempt to give a definite meaning to the term intensity of reflexion.

Imagine a fine pencil of homogeneous† X rays to proceed from a source at A, to be limited by a slit at B, and to be incident upon a crystal C, so placed that a reflected ray is formed which passes into the ionization chamber D. Let the crystal be so adjusted as to give the maximum value of the reflected ray; and let the ionization current in D be measured in the usual way, the current being allowed to run for a stated time, say  $t$  seconds.

We may now remove the crystal and turn the ionization chamber round until the primary beam enters it directly: and we may again measure the ionization current for a given time.

The comparison of these two quantities so obtained does

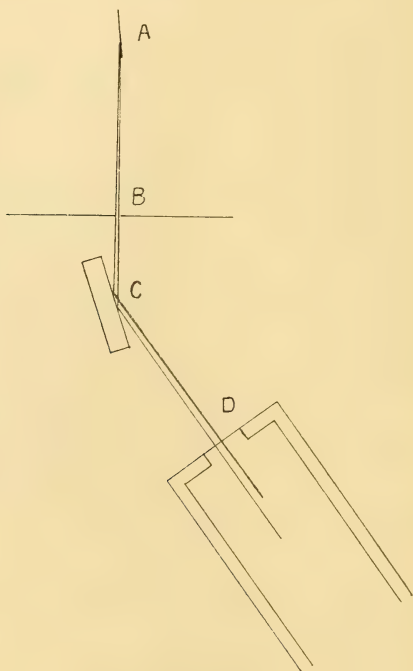
\* *Verh. d. Deutsch. Phys. Ges.* xv. pp. 678, 738, 857 (1913); also *Ann. d. Phys.* 1914, p. 49.

† Homogeneous pencils have been used in these experiments because they are definite, and can be readily obtained intense and pure.



not, however, give us a proper measure of the intensity of reflexion. For, whereas the current in the latter position is proportional to the width of the slit at B, the reflexion in the former case is not proportional to the width of the same slit.

Fig. 1



Reflexion takes place only when the angle between ray and crystal is very exactly adjusted. If we consider the rays which come from a single point in the source at A and fall upon a perfect piece of crystal, a very narrow slit at B will let through all the rays which can be reflected at one time, and the reflexion is not increased by opening the slit any wider. The comparison of quantities will therefore bring in the width of the slit, and it cannot be eliminated without a better knowledge of theory than we possess.

But if we turn the crystal by a succession of small steps through the angle at which reflexion takes place, measuring the ionization current at each step, and if we plot the results in a curve, the area of that curve is a measure of the reflexion effect which *does* contain the width of the slit as a factor. If we open the slit at B we prolong in proportion the range

over which the crystal is able to reflect. When we compare the quantity obtained in this way with the ionization by the direct primary current the width of the slit disappears. Obviously the height of the slit is of no consequence to a first order of approximation. In fact, the ratio is only affected now by the times during which the current is allowed to run in each part of the experiment, and the magnitude of the steps through which the crystal is turned. As these quantities may be kept constant in different experiments, or altered in known proportions, the ratio is now a true comparative measure of the intensity of the reflexion of an X ray of given quality by a given crystal face in a given order\*.

In some measurements I have found it convenient to observe the ionization current for a given time at each step in the movement of the crystal, and subsequently to add together all the currents observed. This is of course equivalent to plotting the curve and integrating it. At other times I have left the rays in action and advanced the crystal one step at each beat of the clock: the movement of the crystal is begun at an angle at which there is no reflexion, it is taken through the reflexion angle, during which time the leaf of the electroscope moves rapidly, and the rays are turned off when the crystal has ceased to reflect. By this method the integration above mentioned is effected automatically. If it were necessary it would be easy to move the crystal at a uniform rate by clockwork, but in practice the simpler methods are quite sufficient for the purpose. The method of steady revolution has been used by de Broglie † in obtaining photographs of the spectra.

\* W. Lawrence Bragg suggests that this principle is capable of still further development. To turn the crystal round at a definite rate is equivalent to submitting it to radiation from all directions for a given time. Let the intensity of primary radiation within a range  $\delta\phi$  be  $R\delta\phi$ , and let  $\delta\theta$  be the angle which the slit subtends at the point source. (It makes no difference to the argument that the source is not a point, but must be treated as an assemblage of points.) When the crystal turns round at the rate  $\omega$ , there will be for a time  $\delta\theta/\omega$  a ray making any desired angle with the crystal. If the crystal stood still and were irradiated from all directions in the one plane (to consider one plane only does not affect the generality) for a given time, then there would be *for that time* a ray making any desired angle with the crystal. The experiment therefore is equivalent to submitting the crystal for a time  $\delta\theta/\omega$  to radiation  $R$  coming from all directions. If  $k$  is the coefficient of reflexion, the intensity of the reflected beam may be put equal to  $k \cdot R \cdot \delta\theta/\omega$ . On the other hand, the measure of the intensity of the primary beam is  $R\delta\theta$ , if it be allowed to enter the ionization chamber for one second. Hence the ratio of the two observed quantities is  $k/\omega$ ; and we find a value for  $k$  in absolute measure.

† C. R. Nov. 17, 1913.

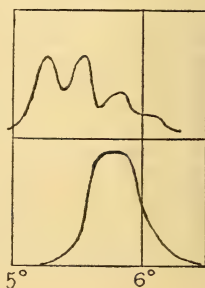
*Phil. Mag.* S. 6. Vol. 27. No. 161. May 1914. 3 N

We may now compare the method of the revolving crystal with the methods by which the earlier measurements of intensity were made. The method then used was to move crystal and ionization chamber together, the latter at twice the rate of the former. In this way a "spectrum" was mapped out, in which the occurrence of "peaks" marked the existence of homogeneous pencils of greater or less strength; and the height of the peak was taken to represent the strength of the reflexion, and used as a means of comparing the relative strengths of various orders of reflexion. This method would be as good as the other *if crystals were perfect*. But they are not. Rocksalt, for example, is very far from being uniform: it consists rather of an agglomeration of smaller and more perfect crystals put together in imperfect alignment. In consequence, a pencil of X rays passing through a fine vertical slit and falling on a vertical crystal face, is not reflected simultaneously at all points of the narrow vertical band along which it meets the crystal. It is reflected first in one part, then in another as the crystal turns round, and one piece of it after another presents itself to the rays at the proper angle for reflexion. Since reflexion does not occur within close limits but is spread over a wide range, the highest point of the peak is much lower than it would be if the crystal were perfect, and is no true measure of the intensity of the reflexion.

For example, the curves of fig. 2 show the result of measuring the intensity of the reflexion of the first order spectrum in the (100) face of rock-salt, the incident rays being limited to a fine pencil. The abscissæ represent the angular positions of the crystal, the ordinates the measured ionization currents. It will be observed how very irregular the curves are; and still more remarkable is the difference between them, for they were obtained from neighbouring portions of the same face. Clearly no measure of intensity is to be obtained from the maximum ordinate of either of these curves. The *areas* of the curves are nearly the same, however. The specimen of rocksalt which was used was very irregular. It is easy to find much better.

If a wide pencil of rays is used the results of irregularities are far less obvious. Portions of the crystal lying on the narrow vertical band above mentioned may not be reflecting

Fig. 2.





when they should, but other portions which lie off the band are reflecting when they should not. The errors average out. But there is an especial risk in using a wide pencil. When the crystal is set at the fine glancing angles of first order reflexion, five or six degrees it may be, there is danger that some part of the pencil may not fall on the crystal face, unless the latter is very wide. It appears probable that in earlier measurements the magnitudes of several first order reflexions were underestimated on this account.

When, however, the newer method is employed, the effects of crystal irregularity largely disappear even when fine pencils are used. Each piece of the face on which the pencil of X rays falls gets its chance in turn, and when all is added up, it is as though the differently set pieces had all acted together. This is a very important consideration.

Although the crystal irregularities prevent all parts of it from acting together, the reflected rays from all parts pass through the slit of the ionization chamber even when it is quite narrow. This curious focussing effect has already been explained in the case of a perfect crystal \*. It is dependent on the equality of the distances from the crystal to the source and to the slit of the ionization chamber respectively. It may be shown that it holds good to a sufficient extent even when the crystal is not perfect. This is a very convenient circumstance, because the slit of the ionization chamber may therefore be set in position to take in the reflected rays of a given wave-length for all positions of the crystal, and at the same time its width may be limited so that there is no chance of other wave-lengths entering the chamber. For instance, there are two strong rhodium lines, and it is easy to use the one and not the other. The stronger line is really a doublet (see below), and in the higher orders it is possible to use one constituent of the doublet and not the other.

One difficulty, apparently of minor importance, should be mentioned : it is easiest to explain it by a numerical illustration. Suppose the glancing angle is  $6^\circ$ , and the crystal has to be turned through the range from  $5^\circ$  to  $7^\circ$  in order to give all parts of the crystal on which the rays impinge the chance of reflecting. Then it is clear that this area is larger when the angle is small ( $5^\circ$ ) than when it has the large value ( $7^\circ$ ). Parts of the crystal are acting in the one case which are not acting in the other. If the crystal were perfect, it must be noticed, this would be quite proper ; but an irregular crystal would only give an approximately true value through averaging. It appears probable, however, that this effect is not

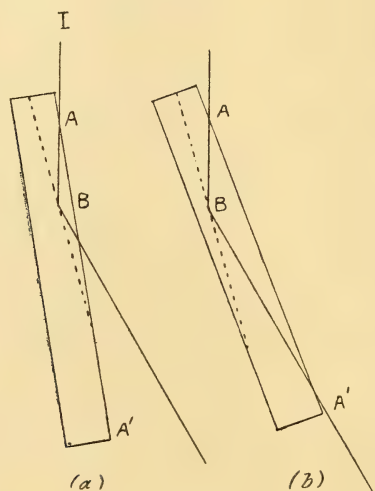
\* Proc. Roy. Soc. lxxxviii. p. 433.



important. Of course it is well to choose for experiment as good a piece of crystal as is possible.

Some of the crystal faces must be prepared, since natural faces are limited in number. A prepared face should be cut so as to be nearly true, say within half or a quarter of a degree. Want of truth makes very little difference in the determination of the angle of reflexion, but may affect an intensity measurement seriously. This may be seen at once from the figure.

Fig. 3.



If the prepared face  $AA'$  is not parallel to the crystal planes, whose direction is shown by the dotted line, it will make a considerable difference whether it is set as represented in (a) or as in (b). The primary pencil  $IA$  enters the crystal at  $A$  and is reduced to a certain value when it reaches  $B$ ,  $B$  being any point on the path and  $AB$  the same length in the two figures. In the one case, however, the reflected pencil has to traverse a much smaller mass of crystal before emerging than it has to do in the other, and the reflexion appears correspondingly greater. This effect is very marked in practice. For example, a (111) face of rocksalt, which reflects the principal rhodium ray at a glancing angle of  $11^\circ$ , was cut  $5^\circ$  out of truth. The intensity of reflexion was then twice as great in the one position as in the other. In the case of a prepared face it is therefore well to measure the intensity effects for both positions and to take the mean, in case the face has not been cut quite truly.

We may now consider some experimental results in the case of rocksalt.

The anticathode A (see fig. 1) was so placed that the rays left it at a grazing angle in order to pass through the slit at B. The slit was half a millimetre wide, and was placed as close to the crystal as possible. The distance from A to B was 17 cm., from B to C 3 cm., from C to D 12 cm. Although the distances AC and CD were not equal, the focussing was sufficiently good. The crystal was turned by hand, five minutes at a time, one movement for each beat of the clock. About three degrees of total movement was sufficient to take in all the reflexion the crystal could give. The rays used were those constituting the principal line of rhodium. To increase the ionization current the chamber was filled with methyl bromide.

The measurements were very consistent, consecutive observations differing by not more than one or two per cent. The results are given in the following table, in which the intensity of the first order reflexion is put equal to 100 and the rest are given as percentages.

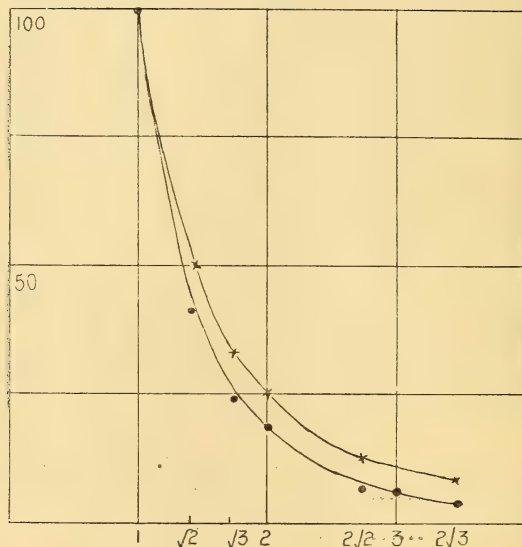
	1st order.	2nd order.	3rd order.	4th order.
Face (100) .....	100	18·7	6·25	
Face (110) .....	41	7·05		
Face (111) .....	16·5	24·4	3·1	4·2

The results for the first two faces show the rapid decline of intensity with increasing order of reflexion which has already been referred to. The planes parallel to the 111 face contain, alternately, sodium atoms only, and chlorine atoms only: as has already been mentioned, the spectra of even orders are therefore much stronger than those of odd orders.

A new experimental fact appears in this, that the intensities of the different faces are comparable with each other. We plot the intensity of each order against the ratio of the sine of its glancing angle to the sine of the glancing angle of the first order of the 100 face. We then find that they all lie nearly on one curve (fig. 4, lower curve), no matter what face they belong to, excepting, however, the first and third spectra of the 111 face. These last, however, are peculiar, and differ from all the others in that they arise from a difference in atomic weights. In the case of sylvine, where potassium has replaced sodium and the weights of potassium and chlorine are nearly equal, these two spectra do not appear.

Considering, therefore, all the reflexions in which the effects of the various atoms add together directly, there is not a different law for each face, but one law for all the

Fig. 4.



faces; and it is of especial interest that those reflexions from the (111) planes, in which the effects of the two kinds of plane add together, fell in with the rest.

It will be observed that the intensities fall away somewhat more rapidly than the inverse square of the sine of the glancing angle. For convenience of comparison, the upper curve in the figure shows how the observed points would have been placed if the law had been that of the inverse square.

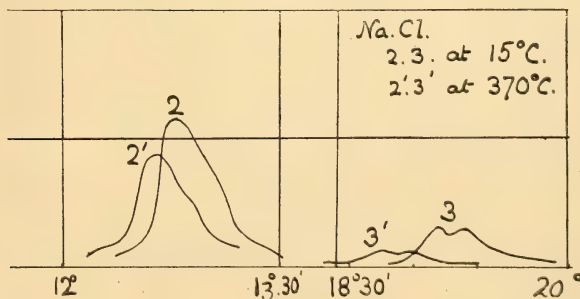
It will be possible eventually to express each of the intensities in the above table in absolute terms, which are independent of all circumstances of the experiment and depend only on the nature of the crystal, the order of the spectrum, or more generally the glancing angle, the temperature, and the wave-length of the rays reflected. This is to be done in the manner explained above (p. 885). I have not attempted to do this so far. It will be necessary to use as primary rays a pencil which has been sorted by reflexion. In these experiments the full stream of rays from a rhodium bulb has been used. Some idea of the efficiency of reflexion may be given by the following experimental results.

A sheet of palladium foil was placed over the slit. The foil cut down the intensity of the principal rhodium line to half value and almost destroyed all the radiations of shorter wave-length than the two rhodium lines. A block of aluminium was added, which still further reduced the principal rhodium line to one seventh. When the primary rays had passed through these screens, the principal rhodium line had fallen to one fourteenth of its first value, the lesser rhodium line would be reduced about half as much, and the rest of the radiation would be very largely absorbed. The primary rays entering the ionization chamber directly then caused a leak of 178 in one beat of the clock. The reflexion current of the first order in the 100 face amounted to 676, when the crystal was turned through five minutes of arc for each beat of the clock. If the primary beam had consisted of the principal line of rhodium only, these figures would have been sufficient to give an absolute value. I hope to give such absolute values in a little time.

The effects of temperature upon the intensity of reflexion have been investigated by surrounding the crystal by a small electric oven. Mica windows permitted the passage of the X rays and stopped convection currents. The results are most conveniently expressed in terms of the ratio of the intensity  $I$  at the temperature of the room to the intensity  $I'$  at the temperature of the furnace. The temperature was measured with sufficient accuracy by inserting into the oven a thermometer the bulb of which was nearly in contact with the crystal.

The ionization currents were observed for each separate position of the crystal. The figure shows the second and

Fig. 5.



third spectra of the rhodium line at each of the two temperatures. The diminution of intensity with temperature is



very obvious; and the spectrum of higher order is more affected than that of lower order. As the crystal expands, the spacing of the planes increases and the glancing angle diminishes. This effect is also clearly seen.

The table shows the variation of the effect with the magnitude of the sine of the glancing angle. The latter is expressed in terms of  $\theta$ , the glancing angle of the first order reflexion by the 100 plane: the value of  $\sin \theta$  is 0.1097.

Face.	Glancing angle.	I/I'.
(100) .....	$1 \times \sin \theta$	1.07
(110) .....	$\sqrt{2} \times \text{,,}$	1.20
(100) .....	$2 \times \text{,,}$	1.26
(110) .....	$2\sqrt{2} \times \text{,,}$	2.07
(100) .....	$3 \times \text{,,}$	1.94

The effects of temperature have been foreseen and calculated by Debije\*, and the figures of the table may be looked on as measurements of the Debije effect.

It is interesting to compare the results given above with the corresponding figures calculated from Debije's formula. The latter may be written in the form

$$I_{\theta} = \frac{A}{\sin^2 \theta} \cdot e^{-B \sin^2 \theta},$$

where A and B are constants, given the crystal, the wavelength, and the temperature, and  $\theta$  is the glancing angle at which the pencil is reflected.  $I_{\theta}$  is the intensity of the reflected pencil.

The constant B contains a quantity which Debije calls the characteristic temperature of the crystal. Its value for rocksalt is not known with certainty, but is believed to be about 240°. In the following table the observed values are set against calculated values. The principal reflexion from the (100) face is always put equal to 100.

The calculated values are slightly modified (become smaller) if we take account of the possible existence of "nullpunkt energie" and of an obliquity factor  $(1 + \cos^2 2\theta)$ , where  $\theta$  is the glancing angle. The two possibilities are considered by Debije (*loc. cit.*). But the figures are hardly accurate enough as yet to bear discussion in respect to these questions.

\* *Ann. der Phys.* 1914, p. 49.

Sine of glancing angle.	Observed values at 15° C.	Calculated, taking $\theta=200$ .	Calculated, taking $\theta=280$ .	Proportional change on raising to 370° C.	Calculated change.
$1 \times 0.1097$ .....	100	100	100	1.07	1.075
$\sqrt{2} \times$ „ .....	41	46.3	47.6	1.20	1.16
$\sqrt{3} \times$ „ .....	24.4	28.5	30.2	—	—
$2 \times$ „ .....	18.7	19.8	21.6	1.26	1.35
$2 \sqrt{2} \times$ „ .....	7.05	7.2	8.9	2.07	1.90
$3 \times$ „ .....	6.25	6.0	7.5	1.94	1.92
$3 \sqrt{3} \times$ „ .....	4.2	3.6	4.9	—	—

On the whole there is certainly a surprising agreement. I find also that fluorspar shows a small temperature effect : this is also in agreement with Debije's theory, for the characteristic temperature is large and the constant B is small.

The diamond is a very perfect crystal, and the intensity curves which are obtained when the crystal is turned round step by step have none of the irregular forms given by rocksalt.

In fig. 6 the points represent the results (uncorrected for inequality of the electroscope scale) of such a series of measurements. The steps are small, there being twelve for every five minutes of arc, and the regularity of the curve which may be drawn through the points is evidence of the regularity of the crystal. The discontinuity on the right-hand side of the curve is due to the double nature of the rhodium line. Fig. 7 shows the first and third spectra side by side, each being the mean of several experiments. The readings of current have been corrected for want of uniformity of the readings of the electroscope. The readings of the third order are magnified five times. The separation of the constituents of the doublet is complete in the higher order spectrum. The two constituents are then separated by twelve minutes of arc. In the figure is shown the result of compounding the two when separated by only four minutes of arc as they are in the first spectrum, and it is seen that the result gives a curve of the experimental form.

The areas of the two curves are to one another as 8.95 to 1. But it must be mentioned that the diamond employed was a thin slip which did not completely absorb the primary rays even when it made an angle with them of only eight and a half degrees. It is not certain therefore that the

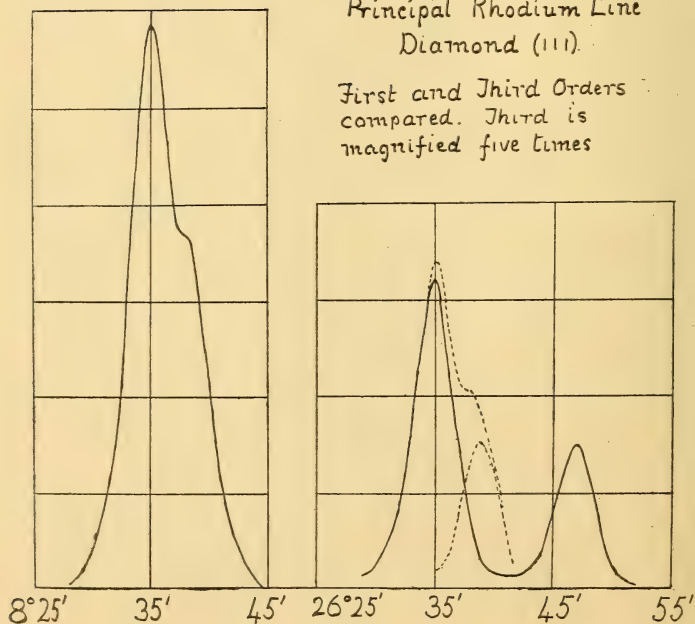
Fig. 6.



Fig. 7.

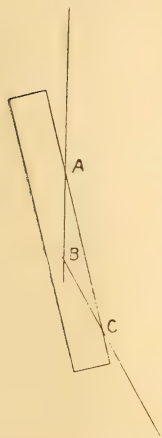
Principal Rhodium Line  
Diamond (111)

First and Third Orders  
compared. Third is  
magnified five times



reflexion obtained was complete; if the crystal had been thicker the reflexion might have been stronger. The point therefore arises as to how the defect is to be calculated.

Fig. 8.



Let us denote the space absorption coefficient of the rays in the diamond by  $\lambda$ . Let the primary rays enter along AB (fig. 8), and the intensity at B be  $e^{-\lambda x}$ , where  $x=AB$  and the primary rays are supposed to have been of unit intensity when they entered. Let  $k\delta x \cdot e^{-\lambda x}$  be the amount reflected while  $x$  is increasing to  $x+\delta x$ . The reflected rays are diminished in the ratio 1 to  $e^{-\lambda x}$  while traversing the distance BC. Thus the intensity of the reflected pencil is

$$\int_0^{x_1} k\delta x \cdot e^{-\lambda x} = \frac{k}{2\lambda} (1 - e^{-2\lambda x_1}),$$

where  $x_1$  is the distance which the primary rays move through the crystal. If the crystal is so thick that  $\lambda x_1$  is large, the intensity of reflexion is  $k/2\lambda$ . If we compare the intensities of reflexion for two different orders, the  $\lambda$  divides out, and the absorption coefficient need not be determined or taken account of. This idea was originally employed by investigators of the scattering which X rays undergo when passing through ordinary materials \*. But if the crystal has a thickness  $t$ , and the glancing angle is  $\theta$ , and if  $\lambda t \operatorname{cosec} \theta (= \lambda x_1)$  is not large, then the reflected pencil has an intensity

$$\frac{k(1 - e^{-2\lambda t \operatorname{cosec} \theta})}{2\lambda}.$$

If we compare the intensities of reflexion in two different orders for which  $\theta$  has different values, the absorption coefficient does not disappear. We must find the value of the factor containing the experimental term before we can obtain a true value for the intensity.

The diamond which I have used was very kindly lent to me by Prof. S. P. Thompson. It is a slip about 6 mm. square and 0.4 mm. thick, its two main faces being cleavage planes. Experiment shows that  $\lambda t$  is equal to 0.81. This makes  $(1 - e^{-2\lambda t \operatorname{cosec} \theta}) = 0.66$  nearly for the first order and 0.33 for the third.

Consequently the true ratio of the intensities of the first and third order reflexions should not be 8.95 to 1, but only half this quantity.

This seems most unlikely, since in the case of all the other

\* For example, by Barkla, Phil. Mag. Feb. 1911.

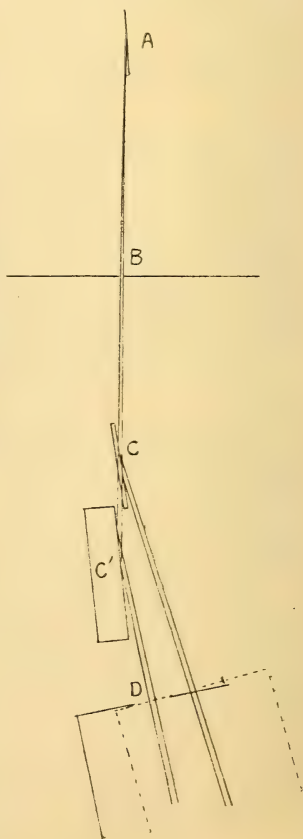


crystals experimented upon the ratio is more than 9 to 1. The intensity in general falls off more rapidly than the square of the sine of the glancing angle.

For this reason I sought for some error in the assumptions. It seemed possible that it might be a mistake to assume the absorption coefficient to be the same when the rays met the crystal at the proper angle for reflexion as when they did not. The strong reflexion which is found experimentally might take place at the expense of the transmitted ray. If this were the case the crystal when reflecting should absorb abnormally: it should be possible to find an absorption band. R. W. Wood found such a band in the analogous case of the reflexion of light by chlorate of potash crystals.

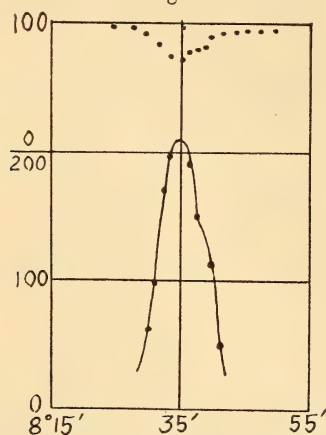
Accordingly the pencil of rays AB was made to pass through the diamond C, which was mounted on the revolving table of the spectroscope, and afterwards to meet a crystal of rocksalt at C'. This was adjusted until it reflected into the ionization chamber through the slit at D. The diamond was then turned very gradually through the angles ( $8^{\circ} 35'$  and  $8^{\circ} 39'$ ) at which it is itself able to reflect. At the same time the strength of the pencil reflected by the rocksalt was continuously observed. It was found that there was a considerable decrease in the intensity of the pencil transmitted by the diamond and reflected by the rocksalt at exactly the angles mentioned. Thus a special absorption *does* exist, and we understand why the attempt to apply a formula in which the ordinary absorption coefficient is used leads to unlikely results. Fig. 10 shows two curves: the upper records the changes in the intensity of the pencil reflected by the rocksalt as the diamond is turned, the lower the changes in the case of the pencil reflected by the diamond. The two sets of measurements are made by

Fig. 9.



means of the same ionization chamber, placed in different positions, as shown in the figure.

Fig. 10.



Absorption band of Rh line  
in diamond (III).

Upper curve shows band  
Lower " " line

The existence of this special reflexion makes it very difficult to interpret the experimental results. The ratio of 8.95 to 1 given above may be explained on the supposition that there is no appreciable temperature effect in the diamond, which would be in agreement with Debye's theory, that the intensity in such case varies as the inverse square of the sine of the glancing angle, and that for the first and third orders the crystal may be treated as infinitely thick. But there may be other explanations. In any case further experiment is needed.

A useful result of a different nature may be derived from the measurements with the diamond. By averaging the large number of observations an accurate value can be found for the difference between the glancing angles of reflexion of the first and third order. The means of two different sets of observations gave  $17^{\circ} 59.8'$  and  $18^{\circ} 00.9'$  respectively: the figures refer to the larger constituent of the doublet. From this we may determine the value of the glancing angle for either order.

When a crystal is mounted on the spectroscope table, it has generally some error of adjustment. This may be corrected by swinging the ionization chamber over to the other

side and turning the crystal through  $180^\circ$ . The glancing angle is the mean of the two values observed. It is probably easier to measure with accuracy the difference between the glancing angles of the first and third orders, as the angular movements are simpler and smaller. But there is an entirely different reason for preferring the latter measure to the former. Where the rays fall on the diamond they penetrate some distance into it, as shown in the figure, and the actual point of reflexion is indeterminate. The reflected pencil is broader than the incident. The angle at which the ionization chamber is set to catch the reflected pencil is a little smaller than if the reflexion took place at the surface, the defect being greater at the smaller angles\*. In the original paper the series of the glancing angles of the first, third, fourth, spectra were found to be  $0.1456$ ,  $3 \times 0.1475$ ,  $4 \times 0.1485$ , and  $5 \times 0.1490$ . The true value of the glancing angle was assumed to be  $0.1495$ .

Fig. 11.



When, however, we turn the crystal round to look for the angle of reflexion, the observed values require no such qualification. The angle at which reflexion takes place is determined by the setting of the crystal table, and the place at which the reflexion occurs is of no consequence. By taking the difference of the settings of the crystal table at the reflexions of the first and third order, we eliminate any error in the placing of the crystal.

Let  $\theta$  be the glancing angle of the first order. We take  $18^\circ 00' 5''$  as the mean of the two angles given above.

We then have

$$\sin(\theta + 18^\circ 00' 5'') = 3 \cdot \sin \theta ;$$

whence  $\theta = 8^\circ 35' 2''$ , and  $\sin \theta = 0.1494$ .

The density of diamond is  $3.520$ . Let  $m$  denote the mass of the hydrogen atom. It has been shown † that there are eight carbon atoms in the elementary cube of side  $2a$  (*loc. cit.*).

Hence

$$(2a)^3 \times 3.520 = 8 \times 12 \times m.$$

$$\therefore 2a = 3.01 \times m^{\frac{1}{3}}.$$

\* Proc. Roy. Soc. lxxxix. p. 279.

† Proc. Roy. Soc. lxxxix. p. 282.

The spacing of the (111) planes

$$\begin{aligned} &= \frac{2a}{\sqrt{3}} \\ &= 1.738 \times m\frac{1}{2}. \end{aligned}$$

Therefore  $\lambda$ , the wave-length of the larger constituent of the rhodium doublet

$$\begin{aligned} &= 2d \cdot \sin \theta. \\ &= 3.476 \times 0.1494 \times m\frac{1}{2}. \\ &= 0.5194 \times m\frac{1}{2}. \end{aligned}$$

If we take  $m = 1.64 \times 10^{-8}$ , we find that  
 $\lambda = 0.614 \times 10^{-8}$ .

*Summary.*

An account is given of experiments in which the intensities of reflected X-ray pencils of various orders are compared with each other, and the results are considered in reference to the recent theoretical discussion by Debye.

It appears that there is a striking agreement between theory and experiment in the case of rocksalt.

The difficulties of experiment with the diamond are also discussed. The existence of an X-ray absorption band in the diamond is demonstrated. The experiments give opportunity for an accurate determination of the wave-length of the rhodium X rays.

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XCVIII. *The Fluorescence of Gases excited by Ultra-Schumann Waves.* By R. W. WOOD and G. A. HEMSALECH\*.

[Plates XIV. & XV.]

**A**N investigation was made a number of years ago by one of the writers, with a view of detecting a possible ultra-violet fluorescence of air excited by waves in the Schumann region †.

A small hole was drilled through a plate of aluminium and condenser-sparks discharged against the under side at the perforated spot. If the region above the plate was photographed with a quartz lens in a dark room, it was found that the air above the hole was emitting ultra-violet light,

\* Communicated by the Authors.

† Wood: "A new Radiant Emission from the Spark," *Phil. Mag.* [6] vol. xx. p. 707 (October 1910).



being excited by radiations of some kind which came from the spark. The luminosity had the form of a narrow vertical jet, and its spectrum, photographed with a small quartz spectrograph, showed the so-called "water-band" of the oxy-hydrogen flame and the ultra-violet bands of nitrogen. The intensity of the radiation was found to be much greater in an atmosphere of nitrogen and much less in one of oxygen. A thin plate of fluorite (1 mm. thick) placed over the hole abolished the phenomenon of the luminous jet completely, from which it was inferred that the excitation was not due to the Schumann waves. It was thought that either luminous molecules were shot out from the spark, or that some sort of corpuscular radiation was responsible for the excitation. The spectrum of the jet was independent of the nature of the metal plate or the lower electrode, and no trace of any of the spark-lines appeared in it, if the gas was free from dust. It was found necessary to exercise great precautions to prevent the formation of dust particles, or nuclei, which scatter the light of the spark, and modify the spectrum of the jet. Metallic dust is given out by the spark, and ultra-violet light causes a cloud to appear in some gases, so that when working in closed chambers, there must be a continuous supply of fresh clean gas.

In the winter of 1910 the writers of the present paper commenced an investigation of the subject but came to no very definite conclusions, though some new and interesting phenomena were discovered. It was found, for example, that if a narrow current of air or dry steam was blown across the luminous jet, the luminosity vanished at the spot traversed by the moving air (or steam) current, but retained its full luminosity both above and below the moving gas stream. It was also ascertained beyond any doubt that the luminous material did not come from the spark, for if a stream of  $\text{CO}_2$ , hydrogen, or coal-gas was directed across the jet, the moving gas current emitted ultra-violet at the point at which it crossed the jet, the spectrum of the emitted light differing in each case. It was also proved that no deviation was produced by a magnetic field.

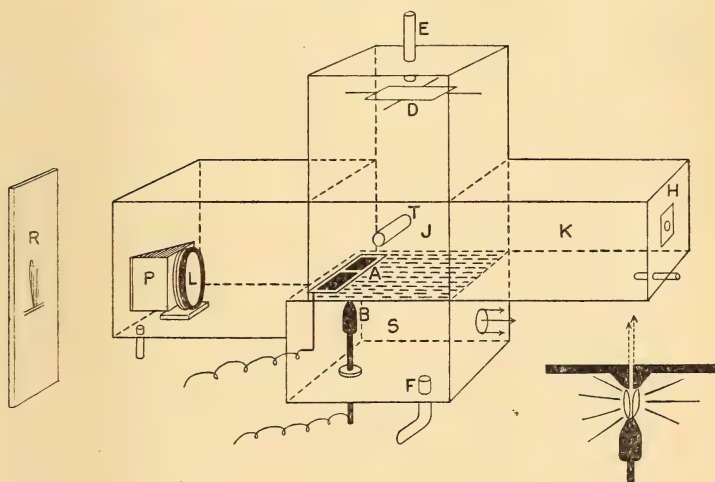
These results were not published at the time, though they were alluded to in a reply (*Phys. Zeit.* xiii. p. 32, 1912) made by one of us to a criticism by Steubing (*Phys. Zeit.* xii. p. 626, 1911), who claimed to have shown that the jet was nothing but light scattered by dust. His experiments were badly carried out in an apparently hasty manner, and he inferred that, since the "water-band" can be found in the spectrum of some sparks, the jet must come from the spark,

i. e. that it is merely the spark aureole projected through the hole.

Steubing's adverse criticism was quite adequately answered at the time. Most of the results which *he* obtained were undoubtedly due to dust particles, which should have been eliminated.

The photographs illustrating this paper, of the jet in different gases, made with a quartz lens through a quartz prism, show that the spectrum differs according to the gas employed. The spark passed always in air in a closed

Fig. 1.



chamber, and the entrance of the other gas was prevented by keeping an excess pressure in the spark-chamber.

We took up the subject anew during the past autumn, and though we have taken over two hundred photographs, we do not feel that we have accomplished much more than to determine the conditions under which future work must be done. We have, however, discovered many extremely curious phenomena, some of which are still quite inexplicable, but which can be reproduced over and over again with absolute certainty. Most remarkable are the effects obtained with moving and stationary gases: some gases showing a much more brilliant fluorescence when moving across the jet of rays from the spark, others responding vigorously to the excitation when quite stagnant, but showing no luminosity

when in motion. The apparatus used in the present investigation is shown in fig. 1.

It was a box constructed of hard wood in the form of a cross, painted black on the inside, and made very nearly gas-tight with putty. The lower compartment S, which will be spoken of as the spark-chamber, communicated with the rest of the box only through the narrow slit at A. This was formed by two jaws of copper about 3 mm. thick, which could be moved to and fro in a brass frame, like the jaws of a spectroscope. The jaws were made of the form shown (in section) by the small diagram of fig. 1, this form being adopted to insure the sparks striking immediately below the slit. If flat plates are used the spark wanders about, and much longer exposures are necessary. The brass frame and copper jaws formed one electrode, the other (B) consisted of a wedge-shaped piece of copper mounted as shown. The rays of the spark come up through the narrow crevice between the jaws, and are absorbed by the black walls of the upper portion of the box. The other compartments of the box were in free communication, the one to the left containing the quartz-fluorite achromatic lens L, and the 30° quartz prism P, which was cemented over a circular hole in the side of the box. This optical system formed a spectrally dispersed image R on the photographic plate of any luminosity produced in the air or other gas above the slit through which the spark rays passed; the compartment K furnished an absolutely black background against which the luminous jet was photographed. When studying the action of moving gas currents on the jet, the current was delivered against the jet by the tube T. The jet-chamber J was filled with the desired gas through the tube E, a shield D insuring thorough washing out of the upper compartment. The spark-chamber was filled through the tube F. Both chambers were connected with a water manometer, so that the pressure in either could be measured. A small window at H enabled observations to be made of the interior, to determine the presence or absence of a visible cloud.

It will be understood that the arrangement of the photographic plate in fig. 1 is diagrammatic only, a small extension camera being arranged for photographing the jets, with its front board removed and the bellows attached to the end of the wooden box. The spark discharge was very powerful, and was furnished by a Hemsalech-Tissot resonance transformer with a condenser of 0.05 mfd. capacity. We usually kept the spark-chamber open on one side, ventilating it with an air blast, which prevented overheating of the electrodes;



the partition between the two chambers was made of brass, which carried off the heat from the jaws of the slit.

For future work we recommend a metal box, of the same general form as the one which we have used; the chambers K and D are essential, as it is necessary to keep the light of the spark away from the background against which the jet is photographed. The position of the lens L should be arranged so that the spectrum of the light from the jaws of the slit is just barely visible in a dark room with an eyepiece.

Small tubes were inserted at the ends of the box to facilitate the washing out of the gases.

The spark-chamber was provided as well with a large hole for the exit of the air, when making experiments with the spark in air. In this way the formation of a cloud of metallic dust was obviated.

It is very important to make sure in each experiment that the "jet-chamber" is free from dust or smoke which scatters all of the light of the spark. In some gases, initially clean, a cloud speedily forms under the influence of the ultra-violet light, and this must be continuously swept away by a fresh supply of the gas. It was found that the faintest cloud visible to the eye, required an exposure of at least three-quarters of an hour to register itself on the photographic plate; and since most of our exposures were of only twenty minutes duration, we could make sure in every instance, that scattered light played no part in our results.

A quartz prism of  $30^\circ$  was placed in front of the quartz-fluorite achromatic lens used for making the photographs. This spreads out the image of the small point of light formed by the illumination of the walls of the narrow aperture through which the spark rays pass, into the short horizontal spectrum, which appears at the bottom of each one of the figures on Pl. XIV. The rays from the spark pass up in the form of a thin sheet, rendering the gas fluorescent, and the monochromatic images of the luminous sheet of gas are separated by the prism, appearing on the plate as vertical streamers of light.

Similar streamers of course appear if the air or gas in the jet-chamber is charged with dust or smoke, but in this case they are located at the regions of the spectrum where the strongest groups of spark-lines fall.

In the photographs which are reproduced on Pl. XIV. the violet region of the spectrum is to the right, the ultra-violet to the left; a small black dot marks the position of the so-called water-band at wave-length 3064. Fig. 1 was made



with oxygen in the jet-box, the streamers being due solely to light from the spark scattered by the cloud of small particles which forms almost immediately in this gas. The presence of scattered light (*i. e.* diffused by dust) can always be recognized by a very intense streamer above the violet region of the spectrum (marked V. in Pl. XIV. fig. 1). It will be observed that this streamer is absent in all the other photographs. Fig. 3, Pl. XIV. was made with  $\text{CO}_2$  in the jet-chamber. Here we have a single streamer practically in coincidence with the left-hand streamer in fig. 1, which is due to the scattering of the strong copper lines 3292 and 3247. Higher dispersion would show this streamer double, the copper lines falling midway between the two bands. Later on we shall refer to the spectrum of the jet in  $\text{CO}_2$  made with a quartz spectrograph.

Fig. 3 shows the jet in nitrogen, the spark-chamber being flooded with oxygen during the exposure. The nitrogen was obtained from a bomb of compressed gas, and contained some oxygen. The strongest streamer, immediately above the black dot, is the so-called water-band, while the three bands to the right (position indicated by vertical lines) are the nitrogen bands. This photograph shows us that the gas in which the spark passes is practically without influence upon the intensity or the spectrum of fluorescence of the gas in the jet-chamber. Very remarkable is the jet shown in fig. 4, also made with nitrogen. In this case the strong streamer to the right appears to coincide with the third nitrogen band (longest wave-length) of fig. 3, which is very faint in fig. 3. In fact, it is doubtful if the nitrogen bands of fig. 3 will appear in the reproduction. Why this streamer is of such great intensity we are unable to say. The previous experiment was, however, made with coal-gas, and we feel inclined to attribute this streamer to some impurity left in the jet-chamber or rubber tube. No trace of the streamer appeared, however, in cases in which the jet-chamber was filled with coal-gas, as appears from fig. 14, Pl. XV., in which we have two streamers, one to the right and one to the left of the position occupied by the water-band.

With a current of hydrogen flowing through the jet-chamber (fig. 16, Pl. XV.), we have a streamer in the same position as the  $\text{CO}_2$  streamer. The hydrogen and  $\text{CO}_2$  were both obtained from bombs, and it is quite possible that some impurity, such as a volatile constituent of the oil used for lubricating the compression-pumps, may be present in each.

It will be impossible to make any very positive statements until the experiments have been repeated with pure gases.

Fig. 11 (Pl. XIV.) shows the water-band streamer obtained with a five minutes exposure when the jet-chamber was filled with nitrogen. With the chamber filled with air and an exposure of twenty-five minutes (fig. 12), we find that the streamer is less intense. The presence of oxygen in the nitrogen may be the cause of the water-band, but if much oxygen is present (as in air) the band is enormously weakened. Strutt has found that the "after-glow" of nitrogen disappears if oxygen is present, and the fluorescence of iodine excited by ultra-violet light is destroyed also by oxygen.

*Fluorescence of Moving and Stationary Gases.*

In our experiments of three years ago an attempt was made to blow the jet to one side by a blast of air, for we were of the opinion at that time that the luminosity might be due to luminous corpuscles projected from the spark, or carried up in the gas blasts projected through the slit by the explosive discharges.

It was found, however, that the air current merely interrupted the jet, the luminosity remaining visible above the moving stream of air. This effect is shown by the photograph reproduced on Pl. XV. fig. 13, made with higher dispersion than the figures previously mentioned. The streamer, which is seen distinctly cut in two by the air-current, is that of the so-called "water-band," the fainter nitrogen bands not showing. The position of the tube delivering the air current is indicated. As we are now quite sure that we are dealing with fluorescence produced by ultra-Schumann waves, it will be unnecessary to speculate about this phenomena from a corpuscular view-point. The air in the moving current was the same as the air in the jet-chamber, and the experiment establishes the fact that air is fluorescent only when it is stagnant. In other words, it seems as though a given mass of air must be acted upon by the radiations from a number of successive sparks to attain its full luminosity. This appears to be true, however, for the water-bands only. For the nitrogen bands the reverse is true: they are brighter if the gas is in motion.

If a current of nitrogen is directed across the spark jet, the water-band streamer is interrupted and a strong patch of luminosity appears displaced towards one side (fig. 5, Pl. XIV.). The direction of the displacement is independent of the direction of the moving current of gas, *i. e.* it is produced by the prism, as is shown by a comparison of figs. 5 and 6. The jet-chamber was filled with the same nitrogen as that which was flowing in a stream across the

jet, yet only the "water-band" streamer shows below and above the moving gas stream. In fig. 7 the nitrogen was flowing out of the tube at a much higher velocity, and the luminosity is very much less, *i. e.* we are beginning to get the effect shown by the water-band streamer with lower velocities. The nitrogen in the jet-chamber was evidently set in violent motion by the high velocity current, and the displaced nitrogen bands are visible as complete streamers, instead of being localized in the moving current as in figs. 5 and 6. We next tried blowing a strong current of nitrogen down against the jet, from a tube inserted in the top of the jet-chamber. Its effect is shown by fig. 8. The water-band streamer is greatly weakened and the nitrogen streamers run up still higher, being almost as intense at the top of the picture where the nitrogen is in rapid motion, as at the bottom where the movement is less violent.

In all cases we found that the time of exposure necessary to record the fluorescent bands of nitrogen could be enormously reduced by keeping the gas in motion. It seems much as if there was a fatigue effect, a flash of fluorescence resulting from the spark radiations, followed by an inability to respond to the radiations from subsequent sparks. It will be remembered that precisely the opposite effect was found for the "water-bands" which disappear entirely if the gas is in rapid motion.

Many experiments have been made to determine the origin of the water-bands. They appeared much stronger in our nitrogen gas than in air, but it must be remembered that our nitrogen contained oxygen. We found, however, that if we added more oxygen to the nitrogen the water-bands were reduced in intensity. If the jet-chamber was filled with oxygen the water-band streamer was exceedingly faint, perhaps  $\frac{1}{20}$  of the intensity which it had in the case of the nitrogen, and no other streamers were visible. A current of coal-gas gave the double band shown in fig. 9.

If a moving stream of oxygen is directed across the jet, the jet-chamber being open on both sides and filled with air, that portion of the water-band streamer which is crossed by the oxygen stream disappears, while a displaced band appears in the same position as the nitrogen band, only much fainter (fig. 10, Pl. XIV). We might attribute this to an impurity of nitrogen in the oxygen, brought out by having the gas in motion, but we must remember that a moving current of air gives no trace of any displaced band. It is quite probable that impurities present in the gases or derived from the rubber tubes through which they passed are responsible for



many of the apparently inexplicable phenomena found in this preliminary investigation.

It appears to be pretty definitely established that oxygen has a tendency to destroy the fluorescence of gases with which it is mixed. This accounts for the extreme faintness of the water-band streamer in oxygen. The oxygen molecules destroy their own fluorescence, so as to speak, the phenomenon being analogous to the one observed by one of us in the case of iodine\*.

A study of the fluorescence of iodine vapour under the influence of the spark rays has been commenced by one of the writers and will be reported in a subsequent paper.

Delivered in a stream of warm nitrogen across the spark-jet it fluoresced with a bluish green light, while if a current of warm *air* was used there was no trace of any fluorescence. If a thin plate of quartz was placed over the slit, the fluorescence was visible for a few seconds and then rapidly faded away. If, however, the quartz plate was moved a little, the fluorescence appeared again. It was found that the opacity of the quartz was produced by an almost imperceptible film deposited upon it by the spark.

We had made many experiments with thin plates of quartz and fluorite, but had failed to find any trace of the water-band streamer, though we obtained faint indications of the coal-gas streamer and possibly those of  $\text{CO}_2$ .

The observations made with iodine threw a new light on the subject and made it necessary to repeat the experiments under conditions which would preclude the formation of the opaque deposit. This was accomplished by moving the quartz plate about during the exposure. Using this precaution the nitrogen streamer was obtained by giving an exposure of only five minutes. Its intensity was equal to that obtained without the quartz plate with an exposure of one minute. No trace of the water-band streamer was found, however.

A fluorite plate 1 mm. thick was next tried, and a faint but unmistakable image of the water-band streamer was obtained with a fifteen minutes exposure. Without the fluorite plate a stronger image of the streamer appeared with a one minute exposure. A rough estimate indicates that the fluorite plate reduces the intensity of the radiations which are responsible for the excitation of the water-band to about 5 per cent. of their original value. This circumstance makes it seem extremely probable that we are dealing with ultra-violet waves much shorter than the Schumann waves, which pass readily

\* Wood & Speas: "A Photometric Study of the Fluorescence of Iodine Vapour," *Phil. Mag.* Mar. 1914, p. 531.



through fluorite lenses and prisms. The radiations which excite the nitrogen bands appear to be reduced to about 20 per cent. of their original intensity after passing through a quartz plate 1 mm. in thickness. Very few experiments have been made with the plates, and the apparatus was not very well adapted to the work, as it is necessary to keep the plates in motion or clean them every ten or fifteen seconds. With a properly designed apparatus it is probable that much more reliable data can be secured. It will also be possible to work with gases at a low pressure, in which case the fluorescence is likely to be very much brighter, judging from the behaviour of iodine, which ceases to fluoresce under the stimulation of visible light when at a pressure of a few millimetres only, its greatest luminosity appearing when it is at a pressure of about 0.2 mm.

A number of photographs of the jet were made with a quartz spectrograph of medium size, an exposure of several hours being necessary. Fig. 15, Pl. XV. shows the spectrum of the jet in nitrogen with a current of nitrogen delivered across the slit. The reduction of the intensity of the water-band, where it is crossed by the nitrogen stream, is very marked. The line to the left of the water-band is the head of the nitrogen band at wave-length 3159. It falls within the less refrangible and fainter portion of the water-band; (see fig. 17 for complete water-band) then come the two strong copper lines 3292 and 3247 (in the continuous spectrum of the light reflected from the slit jaws), then the nitrogen band 3369 (A), and the bands 3527-3576 (B)—3755-3802 (C)—3914 (D).

Fig. 17 was made with a hydrogen current crossing the jet. A faint continuous band appears above the strong copper lines (which show also probably as the result of the formation of a slight trace of fog or cloud, which sometimes happens if a very slow gas-current is used). The water-band is very well shown in this photograph, and can be detected above the region where it is interrupted by the hydrogen stream. In making this experiment the side of the box was opened and the hydrogen allowed to escape without filling the jet-chamber.

Fig. 19 shows the spectrum obtained with a current of  $\text{CO}_2$  blowing across the jet. It appears to be identical with the band found with hydrogen, so far as its position is concerned, but on plates made three years ago the distribution of intensity in the two bands was quite different.

Laboratory of Physical Research,  
Sorbonne,  
Paris.

XCIX. *The Use of the Telephone as an Oscillograph.*  
By Dr. MANNE SIEGBAHN \*.

[Plate XVI.]

1. *Introduction.*

FOR the study of variable currents, instruments are often required to continually register the intensity of the current. It has frequently been proposed to use the telephone for such purposes, as it seems probable that the telephone membrane will reproduce the variations of the current most accurately. Experience shows that even small peculiarities in a person's voice or speech can be recognized through a telephonic transference. There are also a multitude of methods suggested for the registration of the membrane-vibrations, but most of them are not sufficiently sensitive for reproducing the normal amplitude of the telephone-membrane. In a telephone, under ordinary conditions, the amplitude is of the dimension of 0.0001 mm.; and our experience shows that the transference of speech is good only under these circumstances. By increasing the amplitude to such a value that the normal registering apparatus can give measurable deviations, the accuracy of the reproduction will not be the same.

Finally, it is to be remarked that a good acoustical transference does not guarantee that the mechanical vibrations of the membrane are identical with the electrical variations, nor do they even give a sufficiently good copy of them. My own experiments on this subject prove that a very good telephone in the reproduction of sounds, in many respects, causes distortion of the microphone-vibrations.

The following paper deals with the question as to whether a telephone with a normally working current-intensity can be used to register variable currents.

2. *Method for the Registration of the Membrane-vibrations.*

For the above purpose, it is necessary to have a method which can register the vibrations of, say, 0.001 mm. at a maximum with sufficient accuracy. In a paper in *Annalen der Physik*, 1913, pp. 689-728, I have described a method by which it is possible to reproduce the membrane-vibrations with the required accuracy. Since the publication of the

\* Communicated by the Author.

above-mentioned paper, the apparatus have been so much improved that essentially better registrations can be obtained, and the measurements can also be made more accurately. Concerning another method, which may possibly give the same result, see Guyau, *C. R.* 1913, p. 777.

The instrument employed can be seen in fig. 1 (Pl. XVI.). It consists of two coaxial microscopes, the first of which gives a greatly diminished ( $\frac{1}{100}$ ) image of an illuminated slit (1 mm. broad). To the telephone-membrane is attached a sharp edge, which is placed in the image so as to screen off a great portion of the light ( $9/10$ ). The rest of it will pass through the other microscope and form a magnified image on a photographic plate. While the membrane swings, the edge will screen off more or less of the first image, which will cause a corresponding variation in the light-intensity of the image on the plate. On moving the plate perpendicular to the ray of light, there will be sections with different brightness, which will give dark or bright lines on developing the plate.

The darkness of the plate is a measure of the corresponding deviation of the membrane. In order to give a complete representation of the membrane-vibrations, the darkness of the plate must be continually registered. In the above-mentioned paper I have used two methods for that purpose. In the following investigation a variation of these two methods has been employed. The image of a Nernst-lamp-pin was thrown on the plate by means of a cylindrical lens; part of the light will then pass through the plates and fall on a thermopile. The produced thermoelectric force was measured by a self-registering galvanometer (from Hartmann & Braun). On moving the photographic plate slowly in its own direction the galvanometer registers a curve, where the deviations are approximately proportional to the degree of the darkness of the different sections, that is, proportional to the deviations of the telephone-membrane.

There will be faults in the registered curve arising out of the following three factors:—

1. The breadth of the light-line thrown on the plate.
2. The slowness of the thermopile.
3. The free vibrations of the galvanometer-coil.

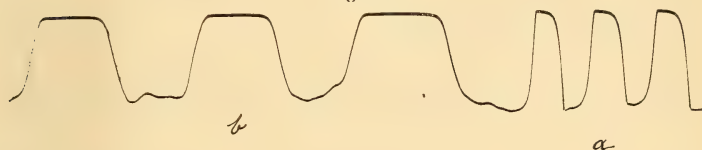
We can understand the effect of these causes, by thinking of a plate with a sudden transition to dark. In letting this section pass over the light-line we shall obtain a slow transition, instead of a sudden one; otherwise, we may receive a



registration with over-lapped vibrations, when the damping of the galvanometer-coil is too small.

I have studied the effect of these three causes separately. The galvanometer was in each case so damped (by introducing a fitting resistance in the second coil-winding) that the aperiodic case was obtained. With very slow speed of the registering drum a sudden current variation was then correctly reproduced. A sudden change of the light-intensity on the thermopile then gives, owing to its slowness, a slow change in the registered curve. The vastness of this effect is seen in fig. 2 *a*, where the light-intensity was suddenly changed with a time-interval of  $\frac{1}{2}$  minute.

Fig. 2.



Finally, the effect of the breadth of the light-line is seen in fig. 2 *b*. On the plate there were three black sections with sharp edges. The correct curve would then have the form of straight lines with right angles. The actual breadth of the light-line can be calculated from this curve.

In reality, this distortion is not so great since such sudden changes are impossible. It may also be helped by diminishing the image, or by drawing the photographic plate with greater speed.

### 3. The Damping of the Membrane.

The damping factor of the system is of the greatest importance in the application of a movable system as oscillographic recorder. As shown by the theories of the ordinary string oscillograph (see the excellent paper on this subject by H. Busch, *Phys. Zs.* 1912), the best results are obtained with a damping factor of 23.14 (the rate of two consecutive amplitudes). This value, however, is deduced under the supposition, that the system vibrates as a simple swinging point, *i. e.*, that it has only one single free vibration. As for the telephone-membrane, we know that there are a series of possible, free vibrations, so that the above theory is not precisely applicable in this case. In my paper in *Annalen* I have indicated a value of 1.14 as the damping factor of the



employed telephone-membrane; this value has later on been verified by new measures. The difference between it and the theoretical value of 23, for the ordinary oscillograph, is remarkable, and gives rise to doubts as to the possibility of using the telephone for oscillographic purposes.

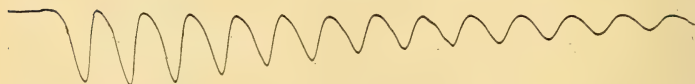
As a theoretical investigation is out of the question, owing to the complicated nature of the phenomenon, we will give some experimental facts, which may serve to throw light on the problem.

#### 4. *The Reproduction of the Currents through the Telephone in more simple cases.*

In figs. 3–11 some oscillograms are shown, taken by the method described above.

Figs. 3 (Pl. XVI.) and 4 give the swinging-curve of the membrane when the curve suddenly changes from one constant value to another; the correct reproduction would then consist

Fig. 4.



of three straight lines, but, as shown in the figure, only the free vibrations of the membrane occur. For such rapid variations the telephone as registering instrument is out of the question.

As the next example, the reproduction of the primary current in an induction-coil with a rotating interrupter is shown in figs. 6–9. The real current-curve (fig. 5) was in

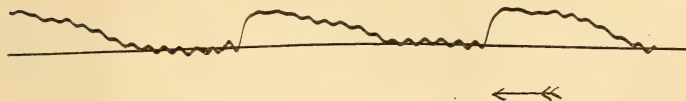
Fig. 5.



this case of the ordinary type of mechanical interrupters, as was controlled by a Braun's tube. The telephone-membrane registers such a curve with a series of overlapped, free vibrations. Thus in this case the obtained curve gives no true copy of the real curve.

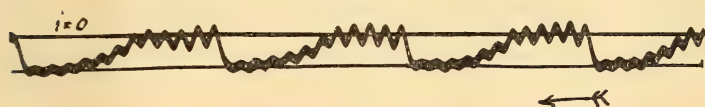
Fig. 6 is registered by means of an ordinary telephone

Fig. 6.



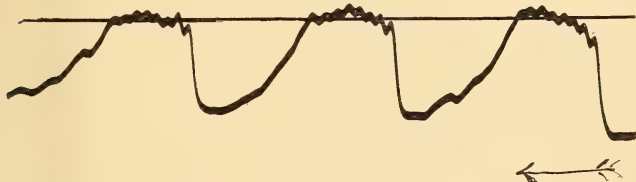
from L. M. Eriksson Telephone Comp., Stockholm. Fig. 7 is taken by means of the same telephone but with a thinner membrane. Both these figures show that the free vibrations

Fig. 7.



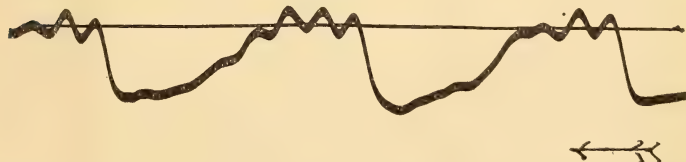
must be suppressed, in order to render a true reproduction possible. To enable us to see whether an electromagnet in damping might diminish the free vibrations, a copper-plate (2 mm. thick) was laid upon the membrane with a thin leaf of mica between them. But, as shown in fig. 8, the damping

Fig. 8.



obtained was, however, insufficient. Then a mechanical damping was tried. The entire telephone was filled with oil. The corresponding registration is reproduced in fig. 9.

Fig. 9.



The result of all this is, that the telephone is not practicable for oscillographic purposes if the registering curves show such rapid variations.

Finally, in the last figures a variable current of lower frequency (about 50 periods per second) is reproduced.

There is no doubt that the general form is fairly correct. But even in this case a detailed accuracy has not been ascertained. In fig. 10 (Pl. XVI.) the vibrations of higher frequency, which arise from the free vibrations of the

Fig. 11.



membrane, can be observed. A measurement of their periods showed that they were engendered by the commutator of the generator. As regards the foregoing examples, it is probable that their amplitudes are greater in the reproduction than they actually are.

As a general result of this investigation, we may state that the telephone can not be utilized for oscillographic purposes.

Örtofta, Dec. 10, 1913.

### *C. Intelligence and Miscellaneous Articles.*

JOHN HENRY POYNTING.

**A**LTHOUGH Prof. Poynting, whose loss will be universally deplored, graduated with high distinction in mathematics at Cambridge, coming out as third wrangler in the tripos of 1876, his interest seems always to have lain in the direct elucidation of physical laws and principles rather than in the evolution and exposition of their consequences by analysis. When he came to Cambridge, in 1872, he was already largely trained in the niceties of refined experimentation; and after graduation he embraced an early chance to resume experimental work at Manchester. The founding of the Mason University College gave him the opportunity of organising a laboratory of his own. Much of his work about this time was concerned with instrumental improvements, such as the design of polarimeters and other apparatus; and to the same period belong studies in chemical physics, such as the elucidation of osmotic pressure, theories to which in later years he returned with conviction, and which, though perhaps not yet fully appreciated, should not be lost sight of, in view of his proved insight into fundamental problems in other domains. An example of the latter is the memoir on the transfer of energy in the electromagnetic field, *Phil. Trans.* 1884, which culminates in the famous result that will go down to posterity as Poynting's Theorem, which not only specifies the path of transfer of electric energy from one material system to another through

the æther, but also as a very special case gives for the first time (strange to say) the dynamical specification of a ray of light.

At about the same time, O. Heaviside, and a little later Hertz, were engaged upon this aspect of electric transmission as an elastic effect propagated from body to body across the æther, in place of the older aspect of electric charges in movement, each carrying its field of disturbance along with it, which, rejuvenated ten years later by exact conceptions of the agency of electrons, duly modified for change of acceleration, now includes the whole field of view. But times not being yet ripe for that, he pursued his subject in 1885 in another *Phil. Trans.* memoir "On the connexion between electric current and the electric and magnetic inductions in the surrounding field," which tracks out the relations of a current circuit by the graphical device of the motion of what are now known as Faraday tubes of force, a type of explanation which is at the present time once more widely in favour.

Afterwards he broke new ground in the experimental determination of the constant of gravitation—the problem of weighing the earth—which had been solved by Cavendish with his accustomed genius by aid of Michell's principle of balancing by torsion. To Poynting's mind an ordinary balance with lever and scale-pans gave at least equal promise of practical accuracy; and his long continued experimental investigations, which were summed up in a *Phil. Trans. Memoir* of 1892 and a Cambridge Adams Prize Essay of 1893, were the starting-point of a new interest in this subject which opened up into many methods more or less cognate to his own. By this time, however, the torsion method had renewed its power through the discovery of the production and properties of quartz fibres by C. V. Boys, whose remarkable subsequent investigation with small-scale apparatus was generously acknowledged by Poynting as the last word on the subject.

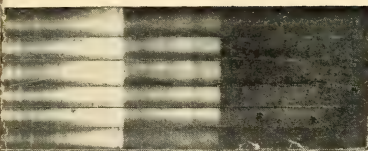



The resource thus acquired in refined dynamical experimenting was to reap further successes in a more untilled field. The ancient idea of a pressure exerted by light, so obvious on the corpuscular view of optics, had been revived by Maxwell on a foundation of an accompanying electric stress in the transmitting medium. Its mere existence, as distinct from an analysis of its propagation to the place where it is in evidence, was already indubitably involved in the Amperean forces on the electric currents induced in the surface of a reflector. It had assumed some importance in its application, notably by FitzGerald, to the elucidation of the mysterious phenomena of comets' tails. To Poynting, this pressure exerted by a ray coming say from a distant star, far out of reach of dynamical effect, involved that the ray carried momentum along with it, and that the pressure effect was of the nature of a thrust exerted along the ray arising from the transfer of this momentum. After long efforts, the disturbances arising from gaseous convection as a whole, and from the radiometric molecular effect were eliminated by Lebedew, and compensated by balancing



against each other by Nicholls and Hull, and the Maxwell value of the direct pressure was fully verified. But Poynting's line of thought led him straight to a tangential component of the thrust as well as a direct component, and he noted that the former could be investigated without much trouble from the gas-effect. This idea led to many beautiful determinations in conjunction with his assistants and students. His idea of convected momentum also led him in another direction to the conclusion that the pressure on a receding surface must be less than on one at rest, so that by reaction a moving radiating body would be accelerated—an impossible result which is corrected by recognizing that its radiation is greater towards the direction of its motion, which leads to retardation on the whole. As the effect depends on extent of surface, it is greater in proportion for small bodies. Thus he was led to consider clouds of cosmic dust revolving round the sun, heated by his rays to an equilibrium temperature of the space where it is, retarded in its motion by the reaction of its own radiation, and thus gradually sucked into the sun. This clearance of solar spaces from dust must be a prominent feature in views of cosmogony. Its calculation aptly illustrates his latent mathematical power, which was never unduly obtruded; and the whole memoir is an example of the simplification of reasoning and reduction to its lowest terms which is a mark of the depth of vision that belongs to genius. When the theory of electrons came to be developed into Maxwell's channels by Lorentz and others, it appeared at once that his stress argument was in default, and the natural first conclusion was against the objective existence of Maxwell's stress as thus specified in favour of one too complex for simple expression. But later Poincaré and Abraham introduced the idea of grouping the outstanding terms as a distribution of electric momentum, specified very simply as the vector product of the æthereal and magnetic inductions. This includes precisely the momentum of radiation elucidated by Poynting. Interest in the subject is thus stimulated, and the problem now under discussion as to whether the residue is in all cases simply momentum, and whence comes the subsidiary travelling inertia which is implied in such momentum, becomes of pressing dynamical interest. An experimental and theoretical incursion into the different field of the elongation of a wire due to its torsion was primarily suggested to Poynting by these problems.

The formulation of an exact notion of the temperature of space, above indicated, is but one phase of his interest in the theory of natural radiation; and it seems but yesterday that he was discussing, in private correspondence, with his usual acuteness and judgment and no sign of failure of powers, the theory of Stefan's law and its other fundamental relations.

J. L.

Concentration of Solution.	Time of Exposure in minutes.	Current in amperes.	Potential	Platinum Hydrate).	Sign.	Potential Difference in volts.	Current in amperes.	Time of Exposure	Concentration of Solution.	
0.001 %	15	0.0258	9		a	+	1720	0.0244	15	0.001 %
0.005 %	15	0.0398	350		b	+	700	0.0400	15	0.005 %
0.01 %	15	0.0412	3		c	+	590	0.0402	15	0.01 %
0.05 %	17	0.0424	2		d	+	400	0.0414	17	0.05 %
0.1 %	15	0.0447	100		e	+	370	0.0424	15	0.1 %
					f	+	200	0.0475	15	0.1 %
				H <sub>2</sub> O bands						
				Sulphuric Acid : 0.75 %.)						
30	0.0007	2	2		a	+	610	0.0392	15	
30	0.0024	2	2		b	-	250	0.0449	15	
				H <sub>2</sub> O bands Pt						
				Sulphuric Acid : 0.03 % ; Hydrate : 0.1 %.)						
15	0.0036				a	-	3200	0.0025	15	
15	0.0033				b	-	256-300	0.0368	15	
15	0.0082				c	-	150-200	0.0386	15	
				Pt Pt						
				Sulphuric Acid : 13 %.)						
30	0.0061				a	-	?	0.0044	11	
17	0.0065									
				Pt						

NOTE.—Where two values are given for the Potential Difference, the higher value occurs during the "bubble formation."



FIG. 1.—(Lithium Hydrate).

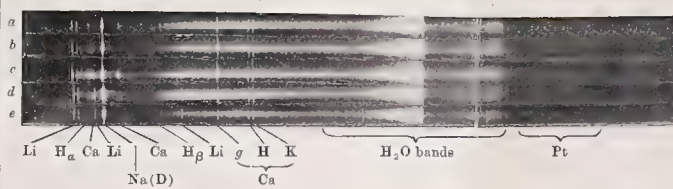


FIG. 3.—(Distilled Water).



FIG. 4.—(Distilled Water).

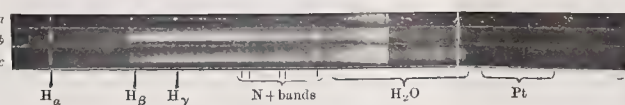
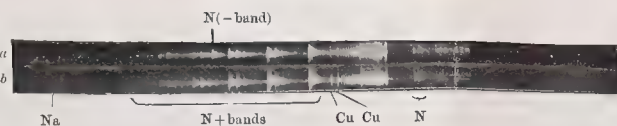
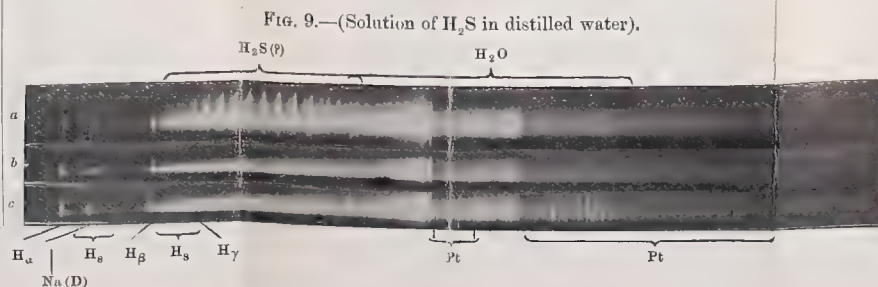


FIG. 5.—(Nitric Acid : .01 %).



Time of Exposure in minutes.	Current in amperes.	Potential Difference in volts.	Sign.
15'	.0175	1000	+
15'	.0045	1950	+
15'	.0053	2200	-



H<sub>α</sub> H<sub>β</sub> H<sub>γ</sub> = Series lines of hydrogen.  
 H<sub>β</sub> = Secondary spectrum of hydrogen.  
 N = Nitrogen bands.

O<sub>K</sub> = Elementary lines spectrum of oxygen.  
 Li = Lithium lines.  
 Na = Sodium lines.

Ca = Calcium lines (H, K, and g of sun's spectrum).  
 Pt = Platinum lines.  
 Pb = Lead lines. Cu = Copper lines.

FIG. 2.—(Lithium Hydrate).

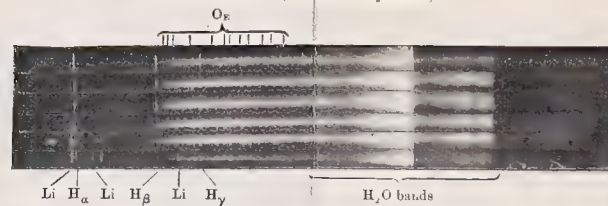


FIG. 6.—(Sulphuric Acid : 0.75 %).

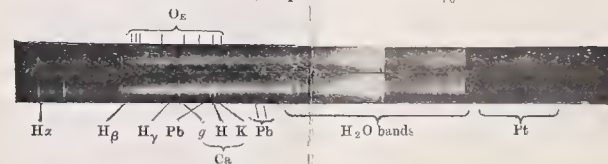


FIG. 7.—(a. Distilled Water; b. Sulphuric Acid : .03 %; c. Potassium Hydrate : .1 %.)

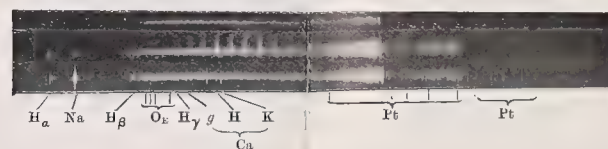


FIG. 8.—(Spark spectrum in Sulphuric Acid : 13 %).



Concentration of Solution.	Time of Exposure in minutes.	Current in amperes.	Potential Difference in volts.	Sign.
.001 %	15	.0258	950	-
.005 %	15	.0398	350-500	-
.01 %	15	.0412	380	-
.05 %	17	.0424	280	-
.1 %	15	.0447	100-200	-

Concentration of Solution.	Time of Exposure in minutes.	Current in amperes.	Potential Difference in volts.	Sign.
.001 %	15	.0214	1720	+
.005 %	15	.0160	700	+
.01 %	15	.0402	590	+
.05 %	17	.0414	400	+
.1 %	15	.0124	370	+
.5 %	15	.0175	200	+

Concentration of Solution.	Time of Exposure in minutes.	Current in amperes.	Potential Difference in volts.	Sign.
.03 %	15	.0392	610	+
.1 %	15	.0449	250	-

Concentration of Solution.	Time of Exposure in minutes.	Current in amperes.	Potential Difference in volts.	Sign.
.03 %	15	.0025	320	-
.1 %	15	.0368	256-300	-
.1 %	15	.0386	150-200	-

Concentration of Solution.	Time of Exposure in minutes.	Current in amperes.	Potential Difference in volts.	Sign.
.13 %	11	.0014	?	-

NOTE.—Where two values are given for the Potential Difference, the higher value occurs during the "bubble formation."

Figs. 1-8 are enlarged about twice from the negatives; fig. 9 about three times. Slight curling of the paper has produced in some cases diffuse lines: fig. 1 ultraviolet portion, fig. 4 and fig. 7 (a). Unfortunately the detail is too poor to show some of the most interesting variations in the spectra; only the more striking variations are indicated. Fig. 7 (b, c) should be compared with fig. 4 (a, b, c); all these spectrograms were taken on the same plate and are from the same enlargement.



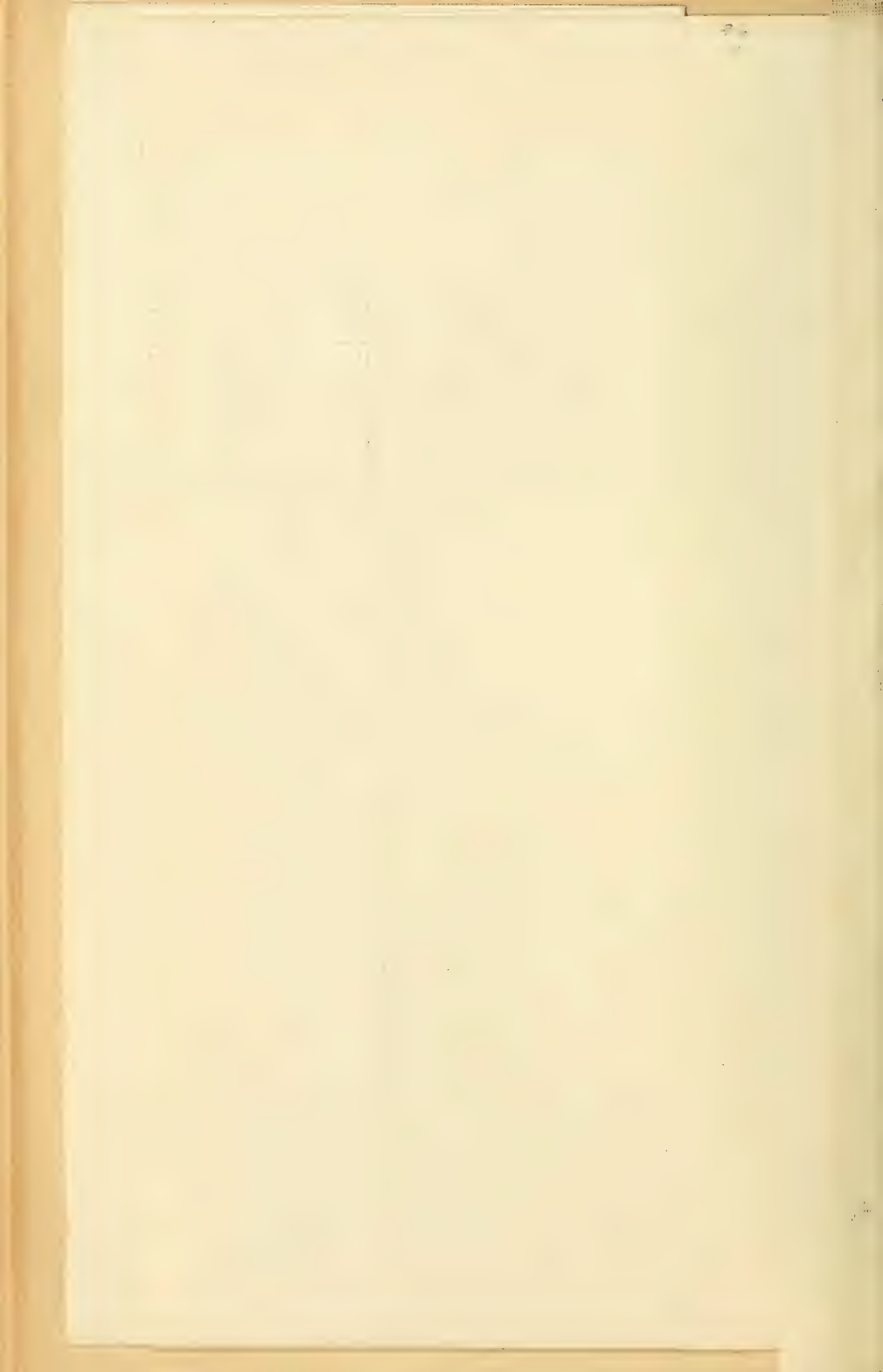
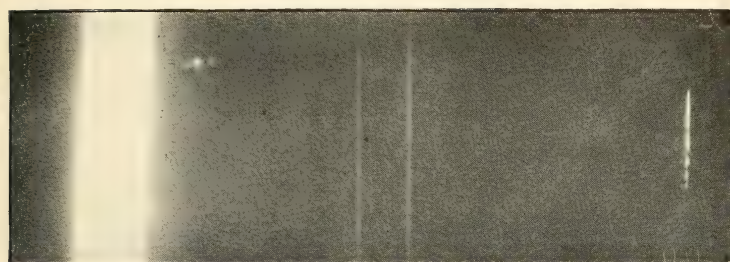


FIG. 2.



B

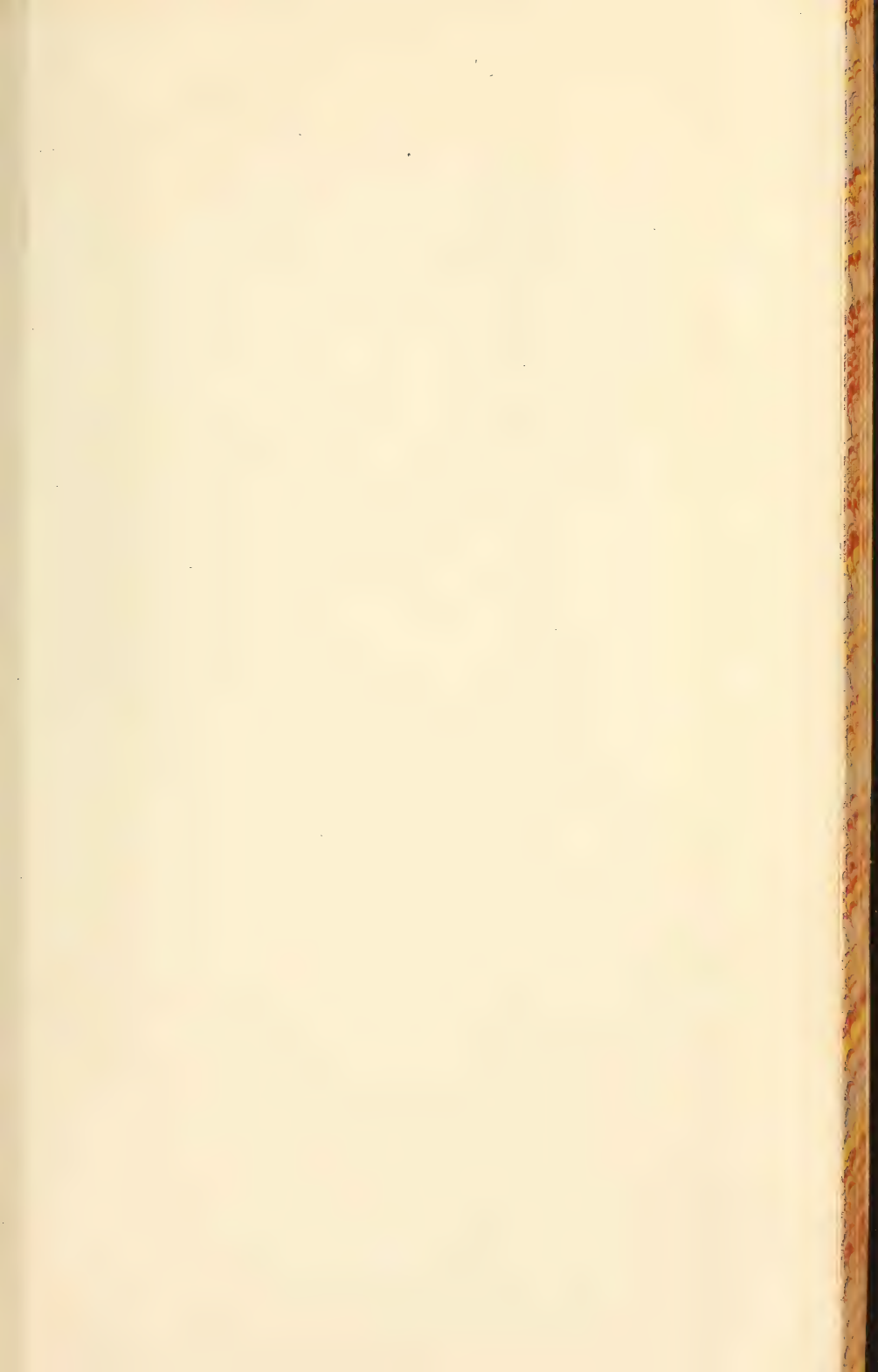
$\beta$   $\alpha$

F

FIG. 4.









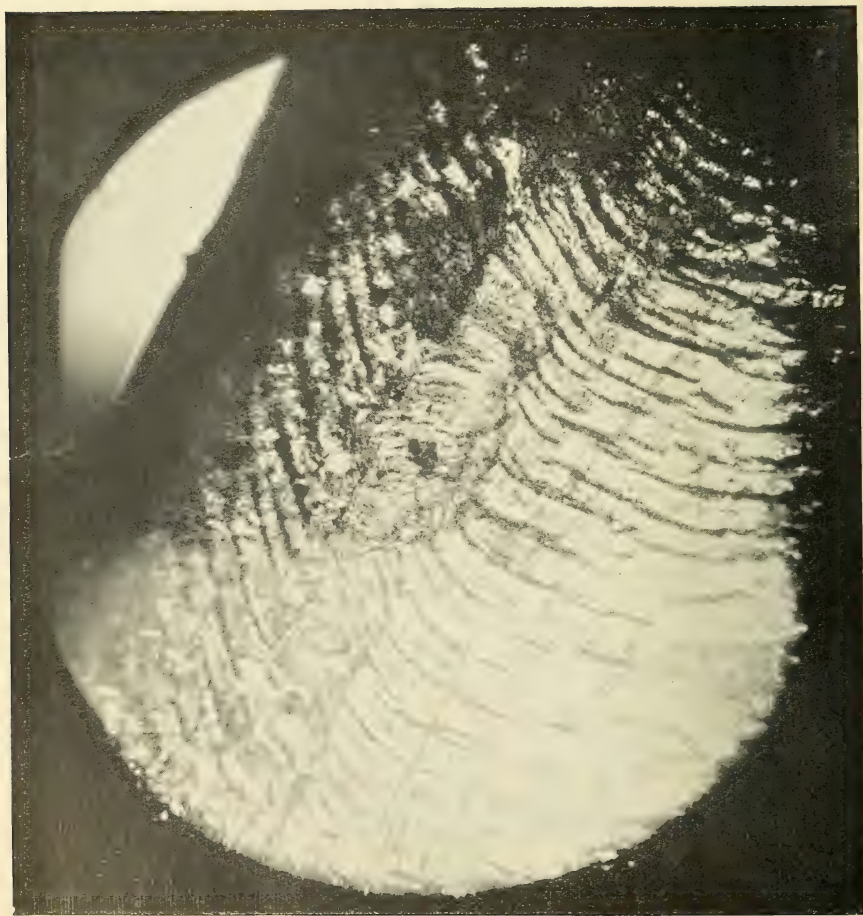


FIG. 4.—Tin. Magnified 130 times.  
(Half breadth of wire shown.)

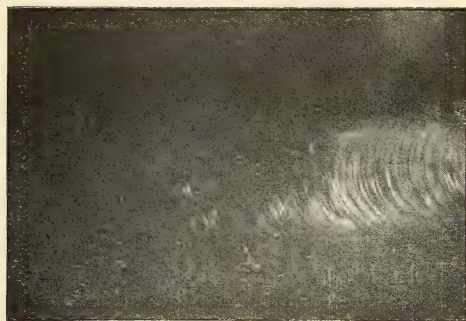


FIG. 1.—Mercury ( $\times 5$ ).

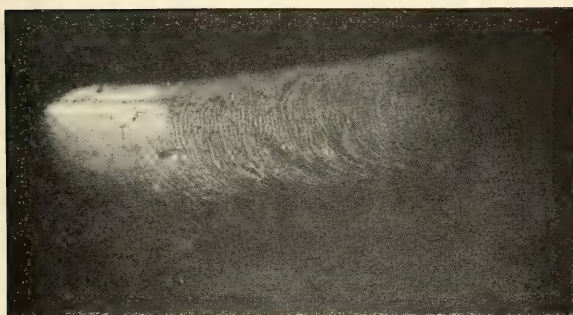


FIG. 2.—Tin ( $\times 10$ ).

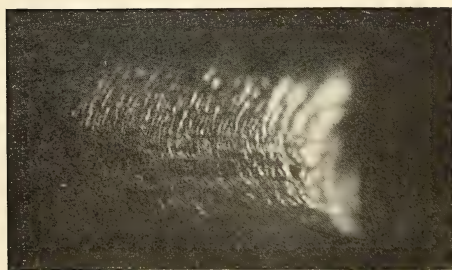


FIG. 3.—Lead ( $\times 10$ ).



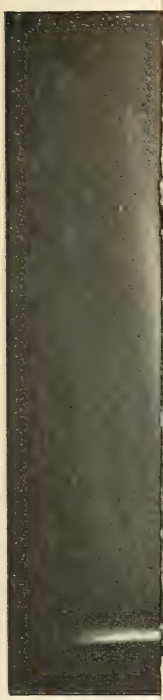


FIG.

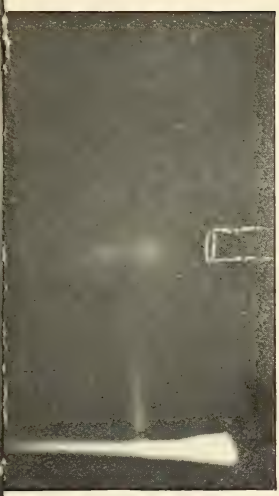


FIG. 9.



FIG. 10.



FIG.



FIG. 11.



FIG. 12.







FIG. 1.



FIG. 2.

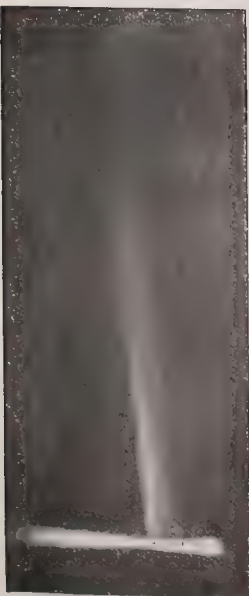


FIG. 3.



FIG. 4.



FIG. 5.



FIG. 6.



FIG. 9.



FIG. 10.



FIG. 7.

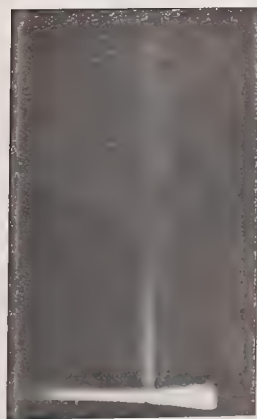


FIG. 8.



FIG. 11.



FIG. 12.







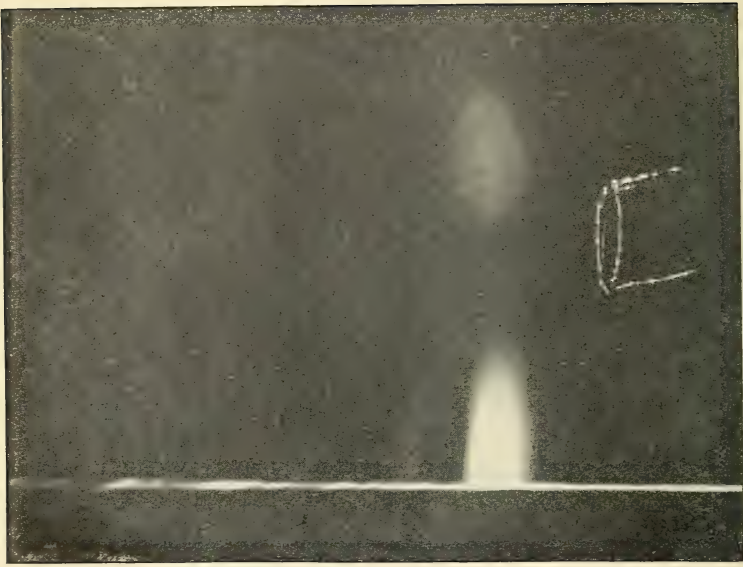


FIG. 13.

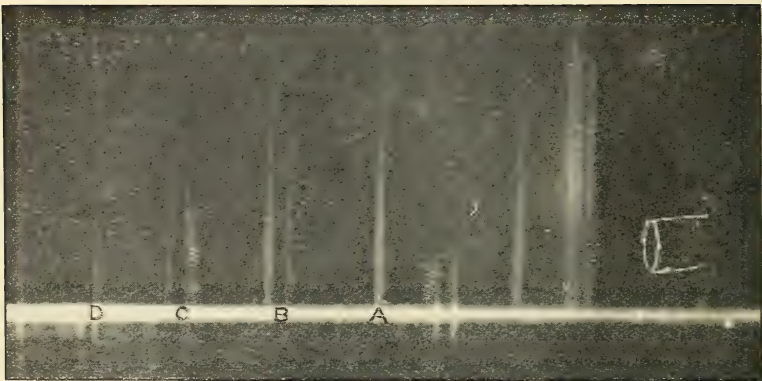


FIG. 15.

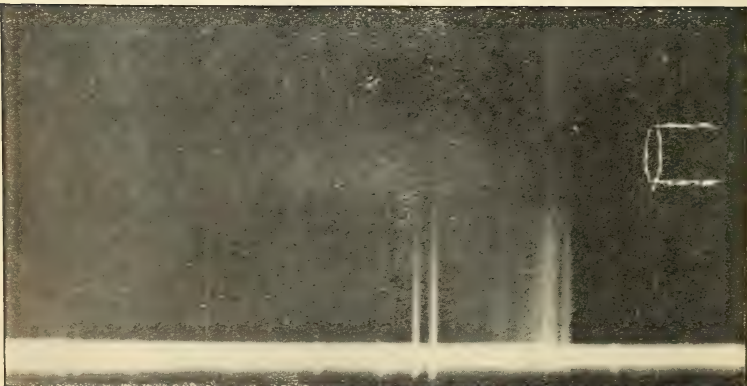


FIG. 17.

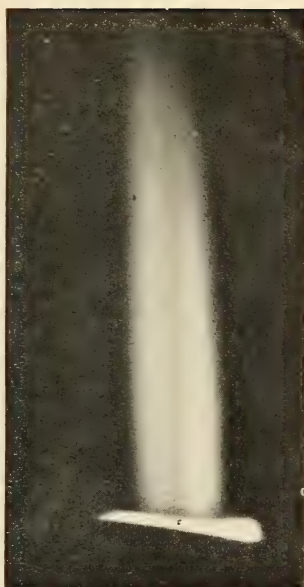


FIG. 14.

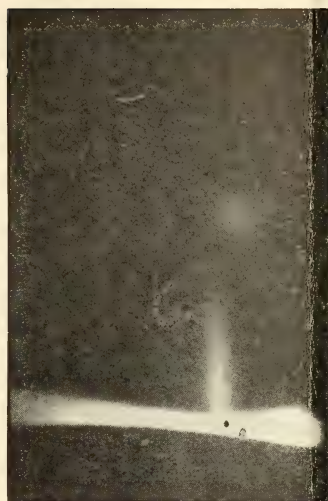


FIG. 18.

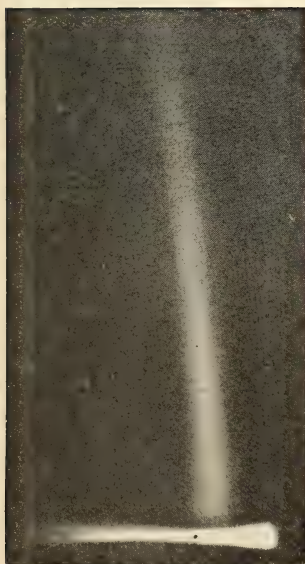


FIG. 16.

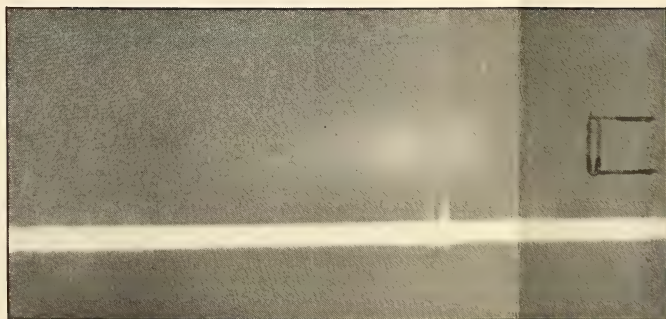


FIG. 19.



FIG. 1.

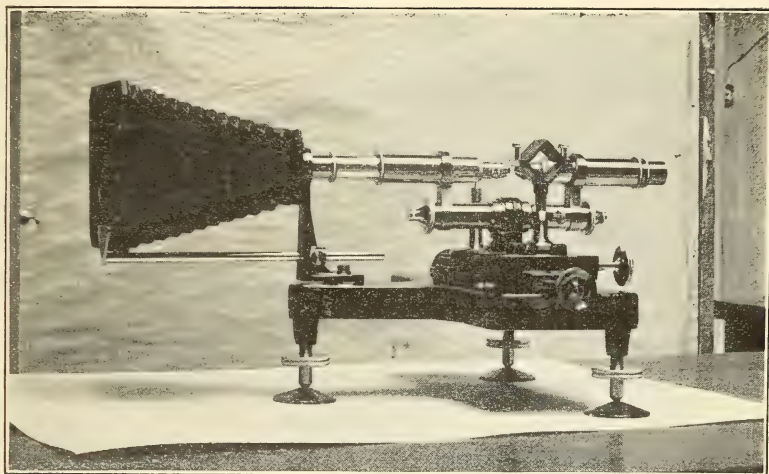


FIG. 3.

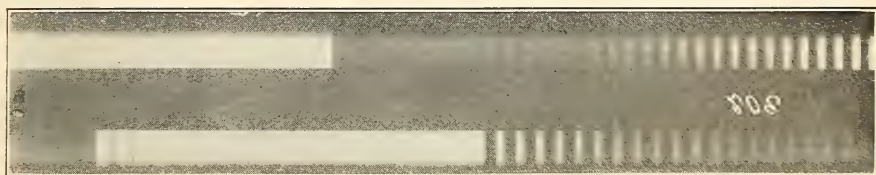
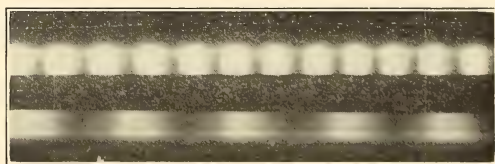


FIG. 10.



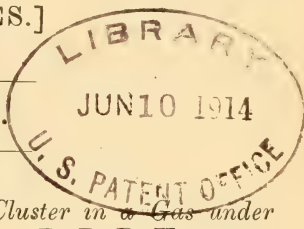




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CI. *The Disintegration of an Ion Cluster in a Gas under the Influence of an Electric Field.* By R. D. KLEEMAN, D.Sc., B.A.\*

WE should expect that the ion clusters in a gas would gradually break up into free ions through being bombarded by neutral molecules, and the free ions gradually become clusters, reasoning from the parallel case of chemical association and dissociation in a gas. The equilibrium between the free ions and clusters would be regulated by the law of mass action and the laws of thermodynamics. It was theoretically investigated, and its bearing on the velocity of ions, &c., in a previous paper by the writer †. It becomes of interest next to investigate experimentally whether the time of process of disintegration of an ion cluster is affected when it is brought under the influence of an electric field. The process of disintegration may be affected by the field in two ways, viz., (a) through increasing the violence of collision of the ion cluster with the neutral molecules, (b) in completing the separation of the elementary ion from its cluster of neutral molecules, which have become separated on collision but which would combine again in the absence of an electric field. In order to fix our ideas let us consider what may happen to an ion cluster in electric fields of different intensities. Suppose, firstly, that the field applied is so weak that the process of disintegration of the cluster remains

\* Communicated by the Author.

† Proc. Camb. Phil. Soc. vol. xvi. pt. iv. p. 285.

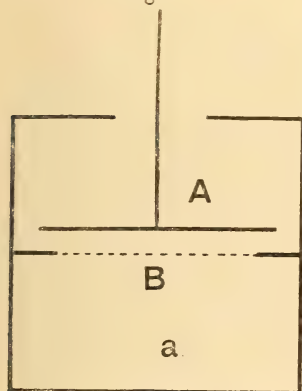
unaltered by the field. The cluster will then pass over a distance  $l$  at the end of which it will have become disintegrated owing to bombardment by the neutral molecules. If the intensity of the electric field is doubled and it still does not affect the process of disintegration of the ion cluster, the distance it traverses before disintegration is  $2l$ , or, generally, under these circumstances the distance traversed is proportional to the intensity of the electric field. But on increasing the electric field sufficiently, a point will be reached when it affects the disintegration of the ion cluster, the distance it traverses being then less than proportional to the electric field. It will be observed that an increase in the electric field at this point still produces an increase in the distance traversed by the ion cluster. On further increasing the electric field, however, a point will be reached when an increase in electric field produces a decrease in the distance traversed by the cluster. The distance then continually decreases with further increase of the electric field. The distance the ion cluster traverses from the instant of its formation to that of its disintegration may be called its free path of disintegration corresponding to the electric field applied. The free path thus passes through a maximum as the electric field is gradually increased. This path is probably not always the same under constant conditions, since the history of the collisions of the cluster with neutral molecules is not always the same, being subject to probability. But there should exist a mean free path about which the different paths are grouped in a similar way as the different paths of a molecule in a gas about its mean free path.

Similar considerations should apply to the free or elementary ions in a gas. Thus there should exist a mean free path of formation of a cluster corresponding to the field applied which depends on the nature of the cluster. This mean free path would be proportional to the field applied over a certain range beginning from zero upwards, while for more intense fields it would be greater. A limiting value of the field would thus exist for which the free ion never forms a cluster, or the mean path is infinite. Ionization by collision probably begins to come in for a field smaller than this limiting value.

The behaviour of ion clusters under the action of an electric field was studied by drawing ions produced in a comparatively weak field through a gauze into a much stronger field, and measuring the current for electric fields of different strengths, including fields sufficiently strong to

produce further ions by collision. This method was previously employed to study the properties of negative and positive elementary ions and clusters\*. The same apparatus was used in these experiments, a full description of which will be found in the last paper quoted. A brief description only will be given here. The ionization chamber consisted of a cylindrical chamber, of which a vertical section passing through its axis is shown in fig. 1. A wire gauze B was in electrical connexion with the chamber and situated at a

Fig. 1.



distance of .5 or 1 cm. from the circular plate A. The rod to which the plate is attached was insulated from the chamber in the usual way, and in electrical connexion with an electrometer. The portion *a* of the gas in the chamber on the lower side of the gauze was ionized by the  $\alpha$  particles from a suitably arranged layer of uranium oxide. On connecting the chamber with a negative or positive potential, negative or positive ions were respectively drawn by the comparatively weak field existing between gauze and chamber-

wall into the much stronger field existing between gauze and plate. The field between gauze and plate was usually gradually increased till of such strength that further ions were produced in considerable quantities by the collision of the free ions with neutral molecules. Some of the ion clusters become elementary ions in the way just described on their passage from gauze to plate. These would at once be seized upon by the electric field and assist in the production of further ions by collision. Therefore on measuring the current between gauze and plate for electric fields of different strengths, information on the behaviour of ion clusters under the action of an electric field may be obtained.

In this paper the results will be described obtained by drawing negative ions through the gauze and measuring the leaks for different fields up to fields of intensity when ionization by collision with positive ions should come in. The investigation is thus a continuation of that described in

\* Proc. Camb. Phil. Soc. vol. xvii. pt. iii. p. 263 ; *ibid.* vol. xvi. pt. vii. p. 621.

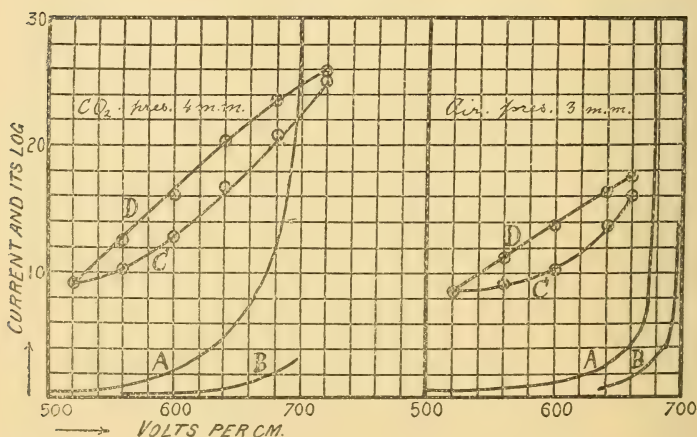


a previous paper. In the present case the magnitude of the currents measured varied over a great range, and in order to deal with them conveniently an air condenser was placed in the circuit connecting the electrometer with the chamber so that the capacity of the system could be varied in the ratios of about from 1 to 9. When it was found necessary to increase the capacity, the current was measured with and without the condenser in the circuit for the same electric field in order to obtain the factor necessary to reduce the readings to the same scale.

*The Disintegration of Clusters through being bombarded by Neutral Molecules.*

When the strength of the electric field is not sufficiently great to assist in the disintegration of the clusters, the number of clusters becoming free ions on their passage from gauze to plate decreases as the field is increased. For the time the clusters take in making this passage, during which they are bombarded by neutral molecules, obviously decreases with increase of field. The increase of current with increase of electric field, supposing new ions are formed by collision of free ions, would then be less than that obtained if no clusters ever became free ions. That such an effect exists, is shown by

Fig. 2.



the curves in fig. 2. The curve A on the left-hand side of the figure shows the relation between currents and electric field

obtained with carbon dioxide at a pressure of 4 mm. of mercury with the negative ions, and the curve B that obtained with the positive ions. The distance  $l$  between gauze and plate was 1 cm. The curve C was obtained on plotting the logarithms (multiplied by 10 for convenience) to the base 10 of the currents obtained with the negative ions against the electric field. On plotting the logarithms (multiplied by 10) of the currents that would be obtained if the total number of ions drawn through the gauze were independent of the field when it is large and no clusters became free ions, we obtain the curve D. This amounts to plotting the values of  $10 \log_{10} n_0 e^{l\alpha}$

or  $(\log n_0 + l\alpha) \frac{10}{2.3}$  for different values of  $\alpha$ , where  $n_0$ , the number of free ions drawn through the gauze, is obtained from the equation  $\log n_0 + l\alpha = 2.3 \log_{10} C_1$ ,  $C_1$  being the current corresponding to the first point in the curve C, and  $l$  the distance between gauze and plate. The values of  $\alpha$ , the collision coefficient for the negative ions, were obtained from the curves connecting  $\frac{X}{p}$  and  $\frac{\alpha}{p}$  given by Townsend, where

$X$  denotes the electric field in volts per cm. and  $p$  the pressure of the gas in mm. of mercury. The figure also shows curves obtained with air at a pressure of 3 mm. of mercury. It will be seen that the slope of the curve D is greater than that of the curve C in both cases. This indicates, we have seen, that the electric field over the region examined does not help to disintegrate an ion cluster; further, that a cluster is gradually disintegrated by being bombarded by neutral molecules. It will also be readily understood from what has gone before that if the disintegration of the clusters is principally due to the effect of the electric field, the curve D would lie below the curve C. A point should therefore exist at which the curve D cuts the curve C. This point is indicated by the trend of the curves in the figure. The number of clusters becoming free ions between gauze and plate at this point is equal to the number becoming free at the starting point of plotting the curves. Since the number of clusters disintegrated between gauze and plate through bombardment by neutral molecules decreases with increase of electric field, the field at the point in question assists to a certain extent in the disintegration of the clusters. The observations from which the curves A, B, and C in fig. 2 have been plotted are given in Table I. The letter L indicates when the current was so large that it could not be measured by the present form of the apparatus.

Carbon dioxide. Press. 4 mm.			Air. Press. 3 mm.		
Field per cm.	Neg. current.	Pos. current.	Field per cm.	Neg. current.	Pos. current.
520	8	3	520	7	
560	11	4	560	8	
600	24	5	600	12	
640	48	6	640	25	8
680	120	20	660	40	10
720	324	...	680	1200	18
...	...	...	690	L	25
...	...	...	696	...	L

We have assumed that the number of ions drawn through the gauze is practically independent of the electric field when it is large. This can be easily proved to be the case. Thus it can be calculated that the electric field in the region where the ions are made is roughly about  $\frac{1}{1000}$  of the field between gauze and plate. Since the pressure of the gas in the chamber is of the order 1 cm., the order of the velocity of the ions in this region is 50. The ions after they are made are therefore subject to recombination only for a period of  $\cdot 1$  of a second, since on the average they have to pass over a distance of about 5 cm. The coefficient of general recombination is approximately proportional to the pressure, and at a pressure of 1 cm. therefore about  $\cdot 01$  that at atmospheric pressure. The chance of an ion combining with an ion of opposite sign is therefore  $\cdot 001$  of its chance at atmospheric pressure. Now when air at atmospheric pressure is ionized by X-rays till a stationary condition is reached and the ionizing agent cut off, it has been found in one particular case that the ionization decreased from 186 to 106 in  $\cdot 45$  of a second or about to one half in  $\cdot 5$  of a second. The ionization per c.c. in the experiments described in this paper was much smaller than the foregoing. It follows, therefore, that the loss of ions by general recombination below the gauze in these experiments was less than  $\cdot 1$  per cent. and therefore of negligible magnitude for fields of the strength used.

But since the ions were produced by  $\alpha$  particles, the effect of initial recombination has to be considered. This species of recombination is largely due to the fact that the ions are produced only along the path of each  $\alpha$  particle, and

consequently they are of great local density. Its magnitude, measured by the lack of saturation between two given fields, would therefore be roughly proportional to the square of the number of ions produced, or proportional to the square of the pressure of the gas. But the coefficient of general recombination varies roughly proportionally to the pressure when it is less than one atmosphere. Thus the lack of saturation due to initial recombination varies as the cube of the pressure. In the experiments described in this paper it would therefore be about  $\frac{1}{4000}$  of what it is at atmospheric pressure and thus small.

In a previous paper we have taken the number of negative ions drawn through the gauze for different fields equal to the corresponding positive leaks. This must lead to erroneous results, since the positive leak increases considerably with increase of electric field. This is due to the fact that ionization by collision occurs even for comparatively weak fields, for the mean free path of an ion must occasionally be so large that the ion acquires sufficient energy under the electric field, even when it is comparatively weak, to produce further ions by collision.

*The Variation of the Velocity of an Ion Cluster with the Electric Field applied when it is large.*

The writer \* has given an equation connecting the velocity of an ion cluster with its period of life during its passage from gauze to plate and other quantities. If  $\eta$  is small in comparison with  $V_1\alpha$ , where  $\eta$  denotes the fraction of the number of clusters per c.c. becoming free ions per second and  $V_1$  the velocity of a cluster, the equation in question becomes

$$C = \left\{ \frac{k_2\eta}{V_1\alpha} + k_1 \right\} e^{-l\alpha}, \dots \dots \dots (1)$$

or  $Ce^{-l\alpha}V_1\alpha = k_2\eta + k_1V_1\alpha, \dots \dots \dots (2)$

where  $C$  is the current measured, and  $k_2$  and  $k_1$  the number of clusters and free ions respectively drawn through the gauze. When only a fraction of the clusters become free ions on their passage over the distance  $l$  between gauze and plate, the condition  $\eta < V_1\alpha$  is satisfied. For  $\frac{\eta k_2}{V_1}$  is then small in comparison with  $k_2$ , or  $\eta < V_1$ , while  $\alpha$  is usually greater than unity except for small values of  $X$ . If the

\* Proc. Camb. Phil. Soc. vol. xvii. pt. iii. p. 269 (1913).



electric field does not assist in the breaking up of the clusters, as is the case in the experiments just described,  $\eta$  is independent of the electric field. Its value is then the same as that it has when negative ion clusters and free ions not under the action of an electric field are in equilibrium with one another. Let us apply the equation to the first and third readings obtained with  $\text{CO}_2$  for the negative ions on the supposition that the velocity of a stable cluster is approximately the same as that of an ion as found in practice, when it goes through a cyclic process during which it is a free ion for a certain time. We then obtain the two equations

$$1.640 \times 10^4 = k_2 \eta + k_1 4.535 \times 10^5,$$

and 
$$1.485 \times 10^4 = k_2 \eta + k_1 6.782 \times 10^5.$$

The velocity of an ion in  $\text{CO}_2$  at a standard pressure for one volt per cm. is taken as  $.85 \frac{\text{cm.}}{\text{sec.}}$ . An inspection of the equations shows that they give  $k_1$  negative, which of course cannot be the case in practice. If we take into account that the number of ions drawn through the gauze might slightly increase with increase of field, the left-hand side of the last equation has to be multiplied by an appropriate fraction, as will be seen on inspecting equation (2). But this will not make  $k_1$  positive. Neither will putting a smaller value for the velocity of a cluster under unit electric field, which amounts to multiplying the numerical quantities in the equations by the same fraction; in fact the value of  $k_1$  is independent of the velocity of a cluster under unit field if it is proportional to the field. The explanation thus appears to be that the velocity of a cluster is not proportional to the electric field for the values of  $\frac{X}{p}$  applying to this case. For, by giving  $V_1$  in the second equation an appropriate value which is larger than the one calculated,  $k_1$  can be rendered positive.

The equations obtained from the first and third readings obtained for air with the negative ion are

$$1.995 \times 10^4 = \eta k_2 + k_1 1.552 \times 10^6,$$

and 
$$1.413 \times 10^4 = \eta k_2 + k_1 2.132 \times 10^6,$$

the velocity of a cluster at standard pressure under an electric field of one volt being taken equal to  $1.87 \frac{\text{cm.}}{\text{sec.}}$ , the velocity obtained for the negative ion in practice. They show that

the same effect exists for air. Thus the velocity of a cluster in  $\text{CO}_2$  is not proportional to the electric field when  $\frac{X}{p}$  has the value 130 and higher values, and the same holds for air when  $\frac{X}{p}$  has the value 173 and higher values,  $X$  being expressed in terms of volts per cm. and  $p$  in terms of mm. of mercury.

*Approximate Evaluation of the Quantities contained in Equation (2).*

Although we cannot in some cases use equation (2) to determine the quantities  $k_2$ ,  $k_1$ , and  $\eta$  in the way described, owing to a want of knowledge of the velocity of an ion cluster for large fields, yet by the help of the equations the order of magnitude of these quantities can be determined. If  $t_1$  denote the period of life of an ion cluster, the number of clusters becoming free ions during their passage from gauze to plate is  $\frac{k_2 l}{t_1 V_1}$ , where  $\frac{l}{V_1}$  is the time the clusters are under way. For two different electrical fields  $X_1$  and  $X_2$ , to which correspond the ionic velocities  $V_1'$  and  $V_1''$ , we then have approximately

$$\frac{k_2 l}{t_1 V_1'} - \frac{k_2 l}{t_1 V_1''} = n_1 - n_2, \quad . \quad . \quad . \quad (3)$$

where  $n_1$  and  $n_2$  denote the number of free ions drawn through the gauze corresponding to the fields  $X_1$  and  $X_2$  calculated on the supposition that no clusters become free ions during their passage from gauze to plate. Since  $t_1 = \frac{1}{\eta}$  \* the equation may be written

$$k_2 \eta l \left( \frac{1}{V_1'} - \frac{1}{V_1''} \right) = n_1 - n_2, \quad . \quad . \quad . \quad (4)$$

and thus gives the order of magnitude of the quantity  $\eta k_2$ . The order of magnitude  $k_1$  may then be determined by means of equation (2). Since  $K = k_2 + k_1$ , where  $K$  denotes the total number of ions drawn through the gauze and is approximately equal to the positive leak obtained, the order of magnitude of  $k_2$  and  $\eta$  can now readily be found. It can be shown by this method that in the case of air, using the first and third readings in Table I., the orders of magnitude of the

\* *Loc. cit.* p. 270.

quantities  $\frac{k_1}{k_2}$  and  $\eta$  for standard pressure are  $10^{-2}$  and  $10^6$  respectively. Similarly it can be shown that in the case of  $\text{CO}_2$  the orders of magnitude of these quantities are  $10^{-2}$  and  $10^6$  respectively.

*Cases in which Equation (2) may be used to Evaluate the Quantities it contains.*

In a previous paper equation (2) was applied to calculate the values of  $\eta$  and  $t_1$  for the clusters in air. It was not examined whether the electric field assisted in the breaking up of the clusters. If this is done in a similar way as described in this paper, it is found that the curves obtained almost overlap, showing that the electric field assists to a certain extent in the breaking up of the clusters. It was therefore thought desirable to obtain data corresponding to lower values of  $\frac{X}{p}$ , and further experiments were therefore carried out with the present form of apparatus. When air dried by being bubbled through strong sulphuric acid at a pressure of 13 mm. of mercury was in the chamber, the leaks 13 and 30 were obtained corresponding to the electric fields of 800 and 910 volts per cm. The corresponding values of  $\alpha$  are 1.3 and 3.0. An examination in the way described shows that the disintegration of the clusters is principally due to bombardment by neutral molecules. We obtain in the same way as before the equations

$$3.834 \times 10^5 = k_2 \eta + k_1 1.082 \times 10^5,$$

$$4.241 \times 10^5 = k_2 \eta + k_1 2.841 \times 10^5.$$

They show that the velocity of a cluster is proportional to the field applied for the fields used in this case. The foregoing equations may therefore be used to calculate  $k_1$ , and give  $k_1 = .233$ . On putting the chamber to a positive potential of 800 volts, a leak equal to 9 is obtained, which is approximately proportional to the total number of ions drawn through the gauze. Therefore  $9 = k_2 + k_1 = k_2 + .233$ , and thus  $k_2 = 8.77$ . About 2 per cent. of the total ions drawn through the gauze are thus in the free state. From one of the above equations we then deduce  $\eta = 4.08 \times 10^4$ . Since  $\eta$  is proportional to the pressure of the air, at standard pressure we have  $\eta = 2.385 \times 10^6$ . If the electric field does not assist in the disintegration of the clusters, as we have seen is the case, the period of life  $t_1$  of a cluster under ordinary conditions

at atmospheric pressure is given by  $t_1 = \frac{1}{\eta}$  and is thus equal to  $4.19 \times 10^{-7}$  sec. If  $\gamma$  denote the fraction of free ions becoming clusters per second in a number of ions in equilibrium  $\gamma k_1 = \eta k_2$ , and thus  $\gamma = 8.98 \times 10^7$  at standard pressure, the ratio  $\frac{k_2}{k_1}$  \* being independent of the pressure. The period of life  $t_2$  of a free ion is given by  $t_2 = \frac{1}{\gamma}$  and thus equal to  $1.11 \times 10^{-8}$  sec.

From the kinetic theory of gases it follows that an air molecule undergoes  $1.6 \times 10^{10}$  collisions per second with other molecules at standard pressure and temperature of  $30^\circ$ . A negative ion cluster therefore undergoes on the average  $6.7 \times 10^3$  collisions before becoming an elementary ion, and an elementary ion undergoes  $1.8 \times 10^2$  collisions before it successfully forms a cluster.

In the application of equation (1) in a previous paper mentioned, the total numbers of ions drawn through the gauze for different fields were taken equal to the corresponding positive leaks obtained, which gives a considerable increase of the numbers in question with increase of electric field. But we have just seen that this is not permissible; the quantity in question is practically independent of the electric field when it is large. A recalculation from the data given in the paper † gives us the equations

$$5.040 \times 10^5 = k_2 \eta + 1.341 \times 10^6,$$

$$5.092 \times 10^5 = k_2 \eta + 1.740 \times 10^6,$$

from which it appears that the deviations of the velocity of a cluster from being proportional to the electric field are not yet so large as to interfere with the calculations. Thus the velocity of a cluster is proportional to the electric field for 77 and lower values of  $\frac{X}{p}$ . From these equations we obtain

$k_1 = .17$ , and hence  $k_2 = 18.33$  since  $k_1 + k_2 = 18.5$ . One of the equations then gives us  $\eta = 1.506 \times 10^4$  corresponding to a pressure of 15 mm. of mercury, and at atmospheric pressure therefore  $\eta = .763 \times 10^6$ . The distance between gauze and plate in these experiments, it should be mentioned, was .5 cm. The value of  $V_1 \alpha$  for one of the fields is

$$\frac{1320 \times 1.87 \times 760 \times 10.73}{15} = 1.3 \times 10^6,$$

and thus large in comparison with  $1.506 \times 10^4$  the value of  $\eta$ , which is the criterion for the applicability of equation (2).

\* *Loc. cit.*

† *Loc. cit.* p. 272.



It will be seen that the value of the quantity  $\eta$ , and the relative values of  $k_2$  and  $k_1$ , are of the same order of magnitude as those obtained in a previous part of this paper. It was found impossible to use equation (2) in the case of  $\text{CO}_2$ , because the velocity of the negative ion cluster was found to be greater than proportional to the electric field for the smallest values of  $\alpha$  obtainable from Townsend's experiments.

*The Disintegration of Ion Clusters through the Action of the Electric Field.*

Results were obtained which show that an electric field applied to an ionized gas helps to disintegrate the clusters if of appropriate strength. It is essential in these experiments to be able to prove that the effect is not due to the positive ions producing further ions by collision. Now the bends in the curves connecting the ionization with the electric field for the negative and the positive ions, which indicate the fields for which a great increase in ionization by collision with increase of field begins to take place, are the further separated the smaller the distance between gauze and plate. The region over which the collision ionization due to positive ions is small in comparison with that due to negative ions thus decreases with this distance. This will appear at once from a consideration of the formulæ for the collision currents for positive and negative ions given by Townsend. In these experiments the distance between gauze and plate was therefore changed to half that in the experiments just described, or made equal to .5 cm. The curve A in fig. 3 shows the currents obtained with the negative ions with  $\text{CO}_2$  at a pressure of 1 mm. of mercury plotted against the electric field, and the curve C shows the product of 10 and the logarithms of the currents to the base 10 plotted against the field. The curve B was obtained by plotting the current against the electric field when the field was reversed, the production of new ions by collision being now initiated by the positive ions. The numbers from which the curves have been plotted are given in Table II. The curve D was obtained on plotting the logarithms of the currents calculated in the way described on the supposition that no ion clusters become free on their passage from gauze to plate. The form of the part *ab* of the curve we have seen indicates that for the corresponding electric fields the ion clusters are principally disintegrated through bombardment by neutral molecules. Since the part *bc* of the curve lies below the curve C, the increase in current observed is greater than if a constant

Fig. 3.

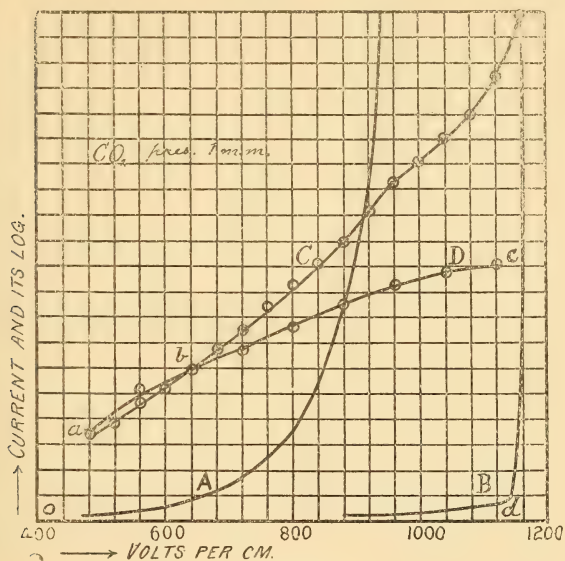


TABLE II.

## Carbon dioxide.

Press. 5 mm.			Press. 2.3 mm.			Press. 1 mm.		
Field per cm.	Neg. current.	Pos. current.	Field per cm.	Neg. current.	Pos. current.	Field per cm.	Neg. current.	Pos. current.
800	20	...	640	15	...	480	5	
840	24	...	720	42	...	520	6	
880	37	...	800	145	...	560	9	
920	48	...	880	182	...	600	11	
960	51	...	920	248	...	640	16	
1000	73	...	960	366	4	680	23	
1040	103	...	1000	519	...	720	32	
1080	158	...	1040	738	...	760	51	
1120	244	...	1080	1152	...	800	74	
1169	370	...	1120	1692	9	840	113	
1200	579	11	1160	2673	...	880	164	4
1240	948	...	1200	4158	...	920	274	
1280	1476	14	1240	6615	20	960	466	
1320	2376	...	1280	12150	27	1000	654	
1360	3672	18	1300	L	36	1040	1092	6
1400	5886	22	1316	...	60	1080	1686	12
1440	9882	126	1320	...	L	1120	3003	
1460	L	L	...	...	...	1160	10857	480
...	...	...	...	...	...	1140	...	16
...	...	...	...	...	...	1152	...	48

initial number of free ions were available for the production of further ions by collision. The fields corresponding to this part of the curve therefore assist in the disintegration of the clusters. The effect cannot be due to the positive ions producing further ions by collision. For it is obvious from the curves A and B that over the region of fields *o d* the number of ions for which a positive ion is responsible or engenders is extremely small in comparison with the number for which a negative ion is responsible. It may of course be argued that the positive ions drawn through the gauze consist of elementary ions and clusters, of which the former only would be immediately available for engendering the production of further ions by collision, and that the bend of the curve B is therefore further from the origin than would be the case if all the positive ions drawn through the gauze were in an elementary state. The evidence that the effect under discussion is due to the breaking up of negative clusters is the fact that it becomes more evident when the ionization by collision of positive ions decreases in comparison with that by negative ions, which, we have seen, is brought about by decreasing the distance between gauze and plate. Further direct evidence that this is the correct explanation will be discussed later.

If we calculate  $n_0$  the number of free ions drawn through the gauze that would account for the total leak corresponding to the field 1120 volts per cm., we obtain

$$n_0 = 3003/e^{.5 \times 13.3} = 3.9.$$

Now the positive leak obtained for the field 880 volts per cm. is equal to 4, and is approximately proportional to the total number of negative ions drawn through the gauze. Since these numbers are nearly equal to one another, it follows that

when the quantity  $\frac{X}{p}$  has reached the value 1120 practically all the clusters get broken up on their passage from gauze to plate.

The velocity of a cluster corresponding to the field 1120 volts per cm. calculated on the supposition that it is the same as that of an ion as measured in practice and proportional to the electric field, is equal to  $760 \times .85 \times 1120 = 7.24 \times 10^5 \frac{\text{cm.}}{\text{sec.}}$

It is however greater, since we have seen that the velocity of a cluster increases at a greater rate with increase of electric field than proportionally to it. It is thus much greater than the average velocity of translation of a molecule

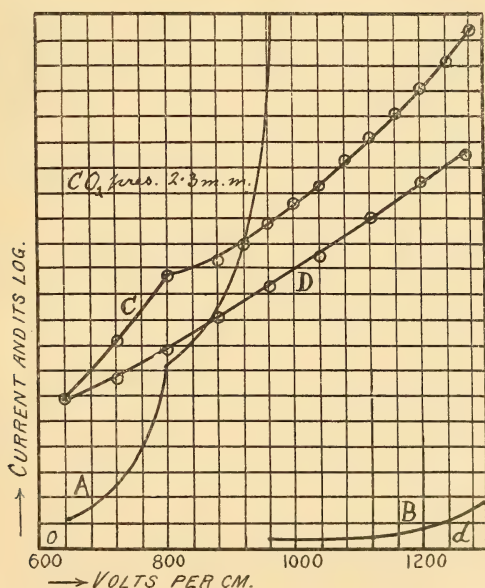
at  $0^\circ$ , which is equal to  $3.96 \times 10^4 \frac{\text{cm.}}{\text{sec.}}$ . Since the ion cluster

gets up momentum during two consecutive collisions, which is reduced on collision, its velocity on collision is very much greater than the average velocity of translation of a molecule.

But some clusters are already disintegrated by the electric field when  $\frac{X}{p}$  has the value 640, which corresponds to the point *b*. The calculated velocity of a cluster is then  $4.1 \times 10^5 \frac{\text{cm.}}{\text{sec.}}$ .

The curves in fig. 4, each of which corresponds to a curve in fig. 3, were obtained with  $\text{CO}_2$  at a pressure of 2.3 mm. of

Fig. 4.

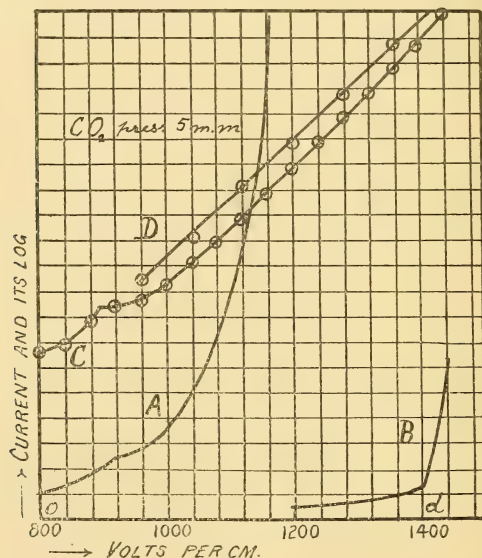


mercury, and the curves in fig. 5 with  $\text{CO}_2$  at a pressure of 5 mm. of mercury. We see that at the pressure 2.3 mm. the disintegration over the region *od* is not so pronounced as at the pressure 1 mm., and at a pressure of 5 mm. the disintegration over that region has practically disappeared. But this is to be expected. For a cluster on the average is



932 Dr. R. D. Kleeman on *Disintegration of an Ion*  
disintegrated through the action of the electric field only  
when the value of  $\frac{X}{p}$  is greater than a certain value, or the

Fig. 5.



kinetic energy of a cluster on collision greater than a certain minimum value, as will be explained more fully further on.

Now the values of  $\frac{X}{p}$  corresponding to the point *d* in these three cases are respectively 1140, 556, and 280, and thus stand in descending order of magnitude. The extent of disintegration of the clusters over the region in question should therefore decrease with these values. Table II. contains the values from which the curves in figs. 3 and 4 were plotted.

The curves A, B, C, and D in fig. 6 were obtained with air at a pressure of 2.3 mm. of mercury. The curve E, corresponding in type to curve C, was obtained with the pressure 3 mm. of mercury. They show that the negative ion clusters in air are disintegrated by an electric field if of appropriate strength. Curves were obtained for different pressures which showed the same characteristics as the curves obtained for CO<sub>2</sub> at different pressures. The curves in fig. 7 were obtained with hydrogen at a pressure of 15 mm. of mercury.

They also show that the negative ion clusters in hydrogen are disintegrated by an electric field if of appropriate strength.

The value of  $\frac{\bar{X}}{p}$  for the first point of the curve C in fig. 6

Fig. 6.

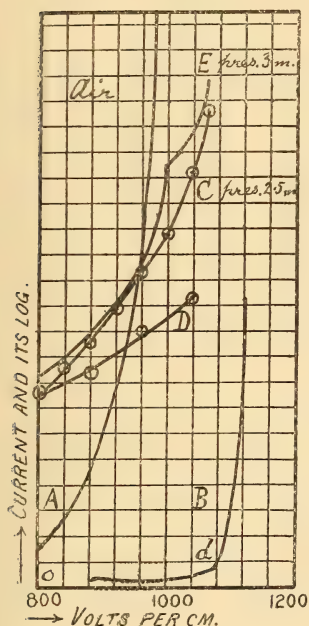
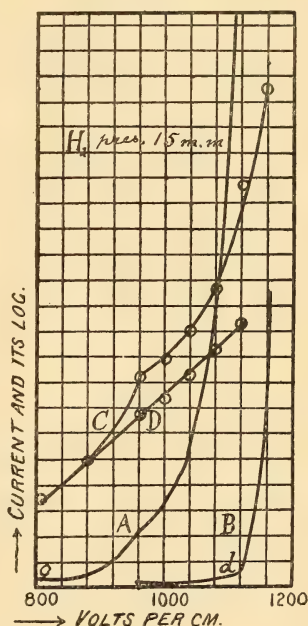


Fig. 7.



for air is 320, and  $4.3 \times 10^7 \frac{\text{cm.}}{\text{sec.}}$  is the corresponding calculated velocity of a cluster. The velocity of translation of a

molecule of air at  $0^\circ \text{C.}$  is  $4.92 \times 10^4 \frac{\text{cm.}}{\text{sec.}}$ . The value of  $\frac{\bar{X}}{p}$

for the first point of the curve C in fig. 7 for hydrogen is 53, the corresponding calculated velocity of a cluster being equal to  $2.6 \times 10^7 \frac{\text{cm.}}{\text{sec.}}$ . The thermal velocity of a molecule at  $0^\circ \text{C.}$

is  $1.859 \times 10^5$ . It appears, therefore, that the velocity of disintegration of an ion cluster is much greater than the average thermal velocity of a corresponding molecule. The distance between plate and gauze in these experiments was .5 cm. The values from which the curves were plotted will be found in Table III.

TABLE III.

Air.						Hydrogen.			
Press. 3 mm.		Press. 2.5 mm.			Press. 6 mm.		Press. 15 mm.		
Field per cm.	Neg. current.	Field per cm.	Neg. current.	Pos. current.	Field per cm.	Neg. current.	Field per cm.	Neg. current.	Pos. current.
800	47	800	33	...	960	16	800	5	
880	78	840	52	...	1040	35	880	10	
920	143	880	85	5	1080	48	960	44	5
960	326	920	152	...	1120	75	1000	63	
980	654	960	294	5	1160	122	1040	106	6
1000	1935	1000	570	...	1200	203	1080	226	
1020	2520	1040	1737	5	1240	386	1120	1470	8
1040	3180	1060	5237	11	1280	1040	1160	7476	
1060	9600	1080	19608	14	1300	2100	1180	18564	
...	...	1100	...	224	1320	5670	1140	...	90
...	...	...	...	...	1340	7686	1152	...	133
...	...	...	...	...	...	...	1156	...	1950

*The Chances of a Negative Ion Cluster disintegrating and of a Positive Ion producing New Ions by Collision.*

The study of the values in Table II. brings out further interesting properties of the negative ion clusters and of the positive ions. It was found that the current, when negative ions were drawn through the gauze, suddenly increased enormously for electric fields in the neighbourhood of the point *d*, for which it will be seen the collision current for the positive ions drawn through the gauze suddenly and rapidly increases. This is evidently due to the positive ions made by the negative ions becoming very efficient in the production of further ions by collision. Since there is a sudden increase in the current over the same region of fields whether positive or negative ions are drawn through the gauze, the initial positive ions must be largely of the same nature in both cases. When negative ions are drawn through the gauze the initial positive ions are in the elementary state, being produced by collision of the negative ions, but when positive ions are drawn through the gauze these ions represent the initial positive ions, and therefore probably consist of elementary ions and clusters of various complexities. These clusters are, however, probably easily disintegrated by the electric field. The sudden increase of the current for the negative ions in question cannot be due to a sudden increase in disintegration of the negative clusters, because it appears apart from the separation of the curves C and D. Compare

fig. 5 with Table II. for example, the separation of the curves C and D is a measure of the disintegration of the clusters which evidently is small over the region *od*. But for stronger fields a sudden increase in the negative and positive current occurs. This indicates that for electric fields of certain strength the chance of a positive ion to produce a new ion by collision per cm. of its path, may be greater than that of a negative cluster to get broken up. This is not at all unlikely. The electron attached to a molecule assumes such a position that its potential energy is a minimum. This would be realized to its greatest conceivable extent when the electron is surrounded by the atoms of the molecule; and an electron getting attached to a molecule would therefore tend to creep inside it. To dislodge the electron the electric field would have to give an amount of kinetic energy to the molecule which would more or less cause it to be broken up by collision with other molecules. This kinetic energy obviously need not have the same value as that which must be given to a positive ion to enable it to produce further ions by collision.

*The Variation of the Chance of Disintegration of an Ion.  
Cluster with the Temperature of the Gas.*

The experiments of E. Gold and H. A. Wilson on the velocity of ions in a flame show that the negative ions are in the elementary state. The temperature of a flame is in the neighbourhood of  $1500^{\circ}\text{C}$ ., and the velocity of a molecule or ion cluster is thus about 2.3 that it has at room temperature. Now we have seen that the velocity that must be given by an electric field to a cluster to disintegrate it at ordinary temperatures is much greater than 2.3 times the velocity of translation. It appears, therefore, that the velocity a cluster must possess in order to become disintegrated decreases with increase of temperature of the gas, whether the velocity of the disintegrating cluster is the result of *temperature* or an *electric field*. Of course, the electric field increases the temperature of a cluster through giving motion to it, but it collides with molecules at a much lower temperature if the gas is at room temperature. But when the disintegration is due to the gas being at a high temperature, the velocity of each colliding body is more or less the same. Also, in the former case the ion cluster constantly loses energy by heat radiation, while in the latter case it receives as much as it loses. Thus the clusters may be in different states internally in these two cases. A change in behaviour of a cluster under an electric field with rise of temperature may therefore be expected.



*Indications as to the Nature of the Negative Ion Clusters in a Gas and the Magnitude of their Mean Free Paths of Disintegration.*

It will have been observed that the curves obtained on plotting the logs of the currents against the electric field show more or less marked kinks. They appear to indicate that for the corresponding electric fields the average or mean free path of dissociation of a cluster is equal to the distance between gauze and plate. We have seen that the mean free path of a cluster should increase with increase of electric field till it reaches a maximum and then decrease. Therefore, when the electric field is very small the average mean free path will lie between gauze and plate. As the field is increased the average path gradually becomes equal to the distance between gauze and plate. Therefore a discontinuity should occur in the current corresponding to this point. This discontinuity is rendered less marked than it would otherwise be by the fact that the clusters drawn through the gauze are in different stages of disintegration through molecular collision, and that the possible free paths of a cluster are not equal to one another but are grouped about a mean free path. The tangent to the current curve at this point would evidently therefore undergo a sudden decrease in value with increase of field. For larger fields than corresponding to this point the mean free path is greater than the distance between gauze and plate, the maximum path defined being in this case greater than this distance. But if the field be sufficiently increased, a point will be reached when the average path is again equal to the distance between gauze and plate. As before, this would be attended by a discontinuity in the current. Thus each kind of cluster drawn through the gauze gives rise to two kinks in the logarithm current curve. These kinks may be called first and second order kinks respectively. From the discussion of the average path, it appears that corresponding to a kink of the first order the disintegration of clusters is principally due to bombardment by neutral molecules, and corresponding to a kink of the second order principally due to the action of the electric field. The effect of ionization by collision is smaller, corresponding to a kink of the first order rather than to a kink of the second order, since the electric field is smaller in the former case, and the former kink should therefore be less conspicuous than the latter. The kinks produced by one kind of cluster would very probably not coincide with those produced by another kind. Thus experiments of the nature carried out might furnish some information on the number of different

clusters that can exist in a gas.. It appears from a study of the curves that the clusters consist largely, if not exclusively, of clusters of one kind. Of course some of the clusters, especially complex ones, might get broken up through the action of the electric field before ionization by collision comes in. The kinks would be absent in this region. The number of such clusters, if they exist, is, however, much smaller than the number corresponding to the one kind of cluster which is conspicuously stable. Thus consider the curve C in fig. 3 for  $\text{CO}_2$ . It shows one kink only, evidently of the second order. The calculated number of free ions drawn through the gauze that would account for the current corresponding to the point *b* is about .02 per cent. of the total number of ions drawn through the gauze. The calculated number of free ions corresponding to the point *d* we have seen is practically equal to the number of ions drawn through the gauze. Thus practically all the clusters become elementary ions over the region *od*, and consist of one kind only since the part of the curve C for this region shows one kink only. The curve C for  $\text{H}_2$  in fig. 7 also shows one kink only which is of the second order. The apparent percentages of the numbers of ions drawn through the gauze which are in the form of clusters corresponding to the fields 800 and 1120 volts per cm. are roughly 95 and 38 respectively. Thus about 60 per cent. of the clusters become free ions over the region *ob*, and consist at least approximately of clusters of one kind. With air at a pressure 2.5 mm. of mercury there appears no kink in the region *od* of the curve C in fig. 6. But when the pressure is 3 mm. of mercury a kink appears, as shown by the curve E in the figure. At a pressure of 6 mm., however, again no kink appears. We shall see presently that the position of the kink on the logarithm current curve for any given cluster varies in a complicated way with the pressure of the gas and the strength of the electric field.

The kinks in the curve, we have seen, indicate when the mean free path of a cluster is equal to the distance between gauze and plate. Thus the mean free path of a cluster in  $\text{CO}_2$  at a pressure of 4 mm. of mercury is equal to .5 cm. when the value of  $\frac{X}{p}$  is equal to 930. At a pressure of 2.3 mm. of mercury the mean free path is equal to the same distance when  $\frac{X}{p}$  has the value 348. When  $\frac{X}{p}$  has the value 64 in hydrogen at a pressure of 15 mm. of mercury, the mean free path is also equal to .5 cm. The disintegration of

the clusters in these cases, we have seen, is principally due to the action of the electric field. Since the mean free path at constant pressure passes through a maximum as the electric field is increased from zero upwards, these mean free paths lie in the region corresponding to the fields which are greater than that corresponding to the maximum path.

The kink in curve C in fig. 5 for  $\text{CO}_2$  at a pressure of 5 mm. of mercury is one of the first order. For since the curve D lies above the curve C the disintegration of a cluster is principally due to bombardment by neutral molecules. The mean free path of a cluster under these conditions is thus  $\cdot 5$  cm. when  $\frac{X}{p}$  has the value 180. The period of life of a cluster in  $\text{CO}_2$  at a pressure of 5 mm. of mercury under ordinary conditions is thus equal to the time it takes to pass over its mean free path. This time is equal to

$$\frac{5 \times \cdot 5}{760 \times \cdot 85 \times 900} = 4 \cdot 3 \times 10^{-6} \text{ sec.,}$$

and the period of life of an ion cluster at atmospheric pressures thus equal to  $2 \cdot 83 \times 10^{-8}$  sec. since it varies inversely as the pressure. But the period of life is less than this value, since we have seen that the velocity of an ion cluster is not greater than proportional to the electric field for fields of the strength used. It seems thus to be considerably less than the period of life of an ion cluster in air at a standard pressure which was found to be of the order  $10^{-7}$  sec. by a different method in a previous part of the paper.

#### *The Effect of Light-Waves on the Stability of a Negative Ion Cluster.*

An experiment was carried out to test whether the negative ion clusters are dissociated by light-waves of much greater wave-length than those waves which constitute ultra-violet light. The light from a Nernst lamp was allowed to pass through a mica window into the gas between gauze and plate and could be cut off at will. But no appreciable difference was observed in the collision current between the light on and off when air was in the chamber. However, other gases will be tried some of which may show the effect looked for. The method is extremely sensitive, thus a change of 1 per cent. of the clusters would about double the collision current.



*Previous Experiments on Negative Ion Clusters.*

In a previous paper the writer has studied the currents when negative ions were drawn through the gauze for fields of different strengths using a large number of different gases. It was found that for the larger number of gases the current, when the effect of ionization by collision became appreciable, could be accounted for by supposing a small fraction only of the ions drawn through the gauze in the free state. The clusters in these gases would thus require, generally speaking, a large field to disintegrate them. The gases which appeared to be exceptional were  $\text{CCl}_4$ ,  $\text{C}_6\text{H}_6$ , and  $\text{CS}_2$ , and the clusters in these gases are thus either disintegrated by a comparatively weak field, or the proportion of free ions to clusters in a number of ions in equilibrium is larger than in the other gases.

*A Formula for the Mean Free Path of Disintegration of an Ion Cluster.*

It will be of interest to obtain a formula for the mean free path of disintegration of an ion cluster. Let  $n_1$  denote the number of chances per cm. of path an ion cluster would have to break up when moving under the action of an electric field, due to being bombarded by neutral molecules. If  $V$  denote the velocity of a cluster under unit electric field, and  $t_1$  its period of life under ordinary conditions, the value of  $n_1$ , if the electric field applied be denoted by  $X$ , is given by  $t_1 n_1 = \frac{1}{XV}$ . Now  $t_1 = \frac{M_1}{p}$ \* and  $V = \frac{M_2}{p}$ , where  $p$  denotes the pressure of the gas and  $M_1$  and  $M_2$  are constants which depend only on its nature, and hence  $n_1 = \frac{p_2}{XM_1M_2}$ . Next

let  $n_2$  denote the number of chances an ion cluster would have per cm. of its path of breaking up due to the action of the electric field. A cluster probably breaks up when the kinetic energy imparted to it by the electric field exceeds a certain maximum value  $E$ . An ion will thus acquire the requisite velocity to disintegrate under the force  $X$  when it travels freely along a distance  $x$  such that  $eXx > E$ , or when  $Xx$  exceeds a certain potential  $P$ . The quantity  $n_2$  then denotes the number of free paths per cm. which exceed the distance  $x$ . In going through the element  $dx$  of these paths the number of chances of disintegration will be proportional to  $n_2 \cdot dx$ , hence  $-dn_2 = kn_2 \cdot dx$ , where  $k$  is a constant. On

\* *Loc. cit.*



integration this equation gives  $u_2 = ce^{-kx}$ , where  $c$  is an arbitrary constant. When  $x=0$  the chance of a cluster getting disintegrated through a single collision with a neutral molecule is unity, hence  $c=N$ , where  $N$  denotes the number of collisions the cluster undergoes in passing over 1 cm., or  $c=N_0p$ , where  $N_0$  denotes the number of collisions at standard pressure. Since  $-x \cdot dn_2$  is the sum of the paths whose lengths are between  $x$  and  $x+dx$ , the sum of all the paths in one cm. is

$$-\int_N^0 x \cdot dn_2 = \int_0^\infty Nkxe^{-kx} = 1,$$

which gives  $k=N=N_0p$ . The value of  $n_2$  is then given by  $n_2 = N_0pe^{-\frac{N_0pP}{X}}$ , putting  $x = \frac{P}{X}$ , the value of the path at the end of which an ion cluster is disintegrated. The number of chances an ion cluster would have of disintegrating in passing over one cm., due to the bombardment by neutral molecules and the action of the electric field, is approximately equal to the sum of the chances of each considered separately, or equal to  $n_1 + n_2$ . The mean free path  $L$  of disintegration of the cluster is the reciprocal of this expression, or

$$L = \frac{1}{n_1 + n_2} = \frac{e^{\frac{N_0pP}{X}}}{N_0p + \frac{p^2}{XM_1M_2} e^{\frac{N_0pP}{X}}} \quad (5)$$

We have seen that it passes through a maximum as the electric field is increased. Strictly, it is the average free path about which all the different paths are grouped according to some law of distribution resembling that applying to the ordinary mean free paths of a molecule. This arises from the fact that the ordinary free path of a molecule is not constant, and that the molecules at any instant in a gas have different velocities. The formula was obtained on the supposition that the velocity of a cluster is proportional to the electric field. This is, however, not likely to hold in most cases, as we have seen.

The period of life  $t_3$  of an ion cluster under the action of an electric field is given by

$$t_3 = \frac{L}{XV} = \frac{e^{\frac{N_0pP}{X}}}{XM_2N_0 + \frac{p}{M_1} e^{\frac{N_0pP}{X}}} \quad (6)$$

It remains constant with increase of electric field till the

field assists in breaking up the clusters, after which it decreases. When the period of life is constant it is the same as that of a cluster not under the action of an electric field and in equilibrium with free ions. In that case  $t_3$  is given by  $t_3 = t_1 = \frac{1}{\eta}$ , where  $\eta$  denotes the fraction of clusters becoming free ions per second of a number of clusters and free ions in equilibrium with one another. The mean free path of disintegration of a cluster under the action of an electric field is then also given by the equation

$$L = \frac{XM_2}{\eta p},$$

or

$$L = \frac{XM_2}{p^2 M_3} \dots \dots \dots (7)$$

since  $\eta = pM_3$ , where  $M_3$  depends only on the nature of the gas.

#### *Summary.*

1. Experimental evidence was obtained that the negative ion clusters in a gas are gradually disintegrated through bombardment by neutral molecules, and consequently a condition of equilibrium is that the free negative ions should gradually form clusters. The average period of life of a negative ion cluster in air not *pecially* dried at atmospheric pressure was calculated to be  $4.2 \times 10^{-7}$  sec. and that of an elementary negative ion  $1.1 \times 10^{-8}$  sec. The corresponding periods of life in  $\text{CO}_2$  were shown to be of the same order of magnitude.

2. Evidence was also obtained that the velocity of a negative ion cluster is greater than proportional to the electric field whose order of magnitude is the same as that producing readily ionization by collision. This is the case in air not *pecially* dried for values of  $\frac{X}{p}$  equal to 173 and higher values, where  $X$  denotes the electric field per cm. and  $p$  the pressure of the gas in mm. of mercury.

3. The negative ion clusters in a gas are disintegrated by an electric field if of sufficient strength through the velocity given to the clusters, the field being of the same order of magnitude as that producing ionization by collision. The magnitude of the effect, like ionization by collision, gradually increases with increase of electric field, which is best shown by curves. It may be stated, however, that the clusters are disintegrated in the case of air,  $\text{CO}_2$  and  $\text{H}_2$  when  $\frac{X}{p}$  has

approximately respectively the values 320, 640, 53, and higher values.

4. It may happen that for a certain pressure of the gas and intensity of electric field the chance of a negative cluster to get broken up in passing over a given distance is less than the chance of a positive ion to produce a new ion by collision.

5. The number of different clusters in a gas is to a certain extent indicated by kinks on a curve. It appears that the majority of negative clusters consist of one kind only.

6. The kinks in the curve enable us to obtain the mean free path of disintegration of a cluster under the conditions of the experiment, that is, the distance a cluster has to run under the electric field before getting disintegrated. Thus, when the disintegration was due to the effect of the electric field, the mean free path was .5 cm. in the gases  $\text{CO}_2$  and  $\text{H}_2$ , corresponding to the pressures 4 and 15, in mm. of mercury, and the fields 3720 and 960, in volts per cm.

7. A theoretical formula for the mean free path of disintegration was deduced.

In conclusion I wish to thank Sir J. J. Thomson for the interest shown in this research, which was carried out at the Cavendish Laboratory. It should also be mentioned that the cost of the air-condenser, and the other part of the apparatus (used previously), was covered by a research grant from the Royal Society.

Cambridge,  
January 20, 1914.

CII. *Contribution to the Thermodynamical Theory of Ternary Mixtures.* By S. A. SHORTER, D.Sc., Assistant Lecturer in Physics in the University of Leeds\*.

CONTENTS.

1. Introduction.
2. General Theory of Chemical Potential in a Ternary Mixture.
3. The Variation of the Chemical Potentials with the Composition of the Mixture.
4. Equilibrium between Liquid and Vapour Phases.
5. Solubility Influence.
6. Osmotic Equilibrium.
7. Partition Equilibrium.
8. The Freezing of Ternary Mixtures.

1. *Introduction.*

THE present paper deals with the purely thermodynamical theory of certain two-phase ternary systems, which have hitherto been studied mainly from a physico-chemical standpoint.

\* Communicated by the Author.

Pure thermodynamics deals, of course, with those relationships between experimental data, which are deducible from the two fundamental laws of thermodynamics, and which are independent, therefore, of any assumption as to the chemical structure of the systems under consideration. The purely thermodynamical theory of a phenomenon is not only interesting in itself, but forms a very desirable preliminary to any chemical theorising. In the case of the systems dealt with in the present paper (as in many other cases) the formulation of chemical theories has preceded the development of the purely thermodynamical theory—an inversion of the natural order of development which has been an abundant source of error.

The method of relating thermodynamically the different phenomena under consideration, adopted in the present work, will be similar to the method adopted in a previous work\* dealing with binary mixtures. The chemical potentials of the components will be regarded as fundamental magnitudes, and in each system studied the experimental data will be related to the potentials. In this way the data will be related to each other in a simple and symmetrical manner.

## 2. *The General Theory of Chemical Potential in a Ternary Mixture†.*

Consider a homogeneous system containing masses  $M_0$ ,  $M_1$ , and  $M_2$  of three components  $C_0$ ,  $C_1$ , and  $C_2$  respectively. Let  $\Phi(M_0, M_1, M_2, p, \theta)$  represent the thermodynamical potential‡ of the system at a pressure  $p$  and temperature  $\theta$ . Let

$$\frac{\partial}{\partial M_i} \Phi(M_0, M_1, M_2, p, \theta) = F_i(M_0, M_1, M_2, p, \theta) \quad (i=0, 1, 2)$$

. . . . (1)

The quantities  $F_i$  are called the chemical potentials of the components. Since  $\Phi$  is a homogeneous function of  $M_0$ ,  $M_1$ , and  $M_2$  of the first degree, we may write

$$\Phi = \sum_{i=0}^{i=2} F_i(M_0, M_1, M_2, p, \theta) M_i. \quad . . . (2)$$

\* Phil. Mag. xxii. p. 933 (1911); xxiii. p. 483 (1912); xxv. p. 31 (1913).

† Duhem, *La Mécanique Chimique*, vol. iii. pp. 1–15, 306, 330.

‡ Gibbs's  $\zeta$  function.



From equations (1) and (2) we can readily deduce the equations

$$M_0 \frac{\partial F_0}{\partial M_0} + M_1 \frac{\partial F_1}{\partial M_0} + M_2 \frac{\partial F_2}{\partial M_0} = 0 \quad . \quad . \quad . \quad (3)$$

$$M_0 \frac{\partial F_0}{\partial M_1} + M_1 \frac{\partial F_1}{\partial M_1} + M_2 \frac{\partial F_2}{\partial M_1} = 0 \quad . \quad . \quad . \quad (4)$$

$$M_0 \frac{\partial F_0}{\partial M_2} + M_1 \frac{\partial F_1}{\partial M_2} + M_2 \frac{\partial F_2}{\partial M_2} = 0 \quad . \quad . \quad . \quad (5)$$

Since

$$\frac{\partial^2 \Phi}{\partial M_i \partial M_j} = \frac{\partial^2 \Phi}{\partial M_j \partial M_i},$$

we have

$$\frac{\partial F_1}{\partial M_2} = \frac{\partial F_2}{\partial M_1} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$\frac{\partial F_2}{\partial M_0} = \frac{\partial F_0}{\partial M_2} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\frac{\partial F_0}{\partial M_1} = \frac{\partial F_1}{\partial M_0} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Now the chemical potentials are homogeneous functions of  $M_0$ ,  $M_1$ , and  $M_2$  of zero degree, and hence can be written in the form  $f_i(s_1, s_2, p, \theta)$  ( $i=0, 1, 2$ ), where  $s_1=M_1/M_0$  and  $s_2=M_2/M_0$ . From the above equations we can readily deduce the equations

$$\frac{\partial f_0}{\partial s_1} + s_1 \frac{\partial f_1}{\partial s_1} + s_2 \frac{\partial f_2}{\partial s_1} = 0, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$\frac{\partial f_0}{\partial s_2} + s_1 \frac{\partial f_1}{\partial s_2} + s_2 \frac{\partial f_2}{\partial s_2} = 0, \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$\frac{\partial f_1}{\partial s_2} = \frac{\partial f_2}{\partial s_1} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Consider two homogeneous systems, the one containing masses  $M_0 + \delta M_0$ ,  $M_1 + \delta M_1$ ,  $M_2 + \delta M_2$ , and the other masses  $M_0 - \delta M_0$ ,  $M_1 - \delta M_1$ ,  $M_2 - \delta M_2$  of the components  $C_0$ ,  $C_1$ , and  $C_2$  respectively. Unless the equations

$$\frac{\delta M_0}{M_0} = \frac{\delta M_1}{M_1} = \frac{\delta M_2}{M_2} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

are verified, the two systems will differ in composition, and if they are placed in communication with each other, diffusion will occur and finally a homogeneous system will result. This irreversible process must result in a diminution

of the thermodynamical potential, so that provided equations (12) are not verified, we must have

$$\begin{aligned} \Phi(2M_0, 2M_1, p, \theta) < \Phi(M_0 + \delta M_0, M_1 + \delta M_1, M_2 + \delta M_2, p, \theta) \\ + \Phi(M_0 - \delta M_0, M_1 - \delta M_1, M_2 - \delta M_2, p, \theta) \\ \dots \dots \dots (13) \end{aligned}$$

From this inequality we can readily deduce the following inequalities :

$$\frac{\partial F_0}{\partial M_0} > 0, \quad \dots \dots \dots (14)$$

$$\frac{\partial F_1}{\partial M_1} > 0, \quad \dots \dots \dots (15)$$

$$\frac{\partial F_2}{\partial M_2} > 0, \quad \dots \dots \dots (16)$$

and also three inequalities of the form

$$\frac{\partial F_i}{\partial M_i} \frac{\partial F_j}{\partial M_j} - \left( \frac{\partial F_i}{\partial M_j} \right)^2 > 0 \quad (i \neq j) \quad \dots \dots \dots (17)$$

Expressing the chemical potentials in terms of the concentrations  $s_1$  and  $s_2$ , we readily obtain the inequalities

$$\frac{\partial f_1}{\partial s_1} > 0 \quad \dots \dots \dots (18)$$

$$\frac{\partial f_2}{\partial s_2} > 0 \quad \dots \dots \dots (19)$$

$$\frac{\partial f_1}{\partial s_1} \frac{\partial f_2}{\partial s_2} - \left( \frac{\partial f_1}{\partial s_2} \right)^2 > 0 \quad \dots \dots \dots (20)$$

In my previous work on binary systems I used, as far as possible, special symbols for the differential coefficients of the chemical potentials. I shall adopt a similar plan in the present work, using the following special symbols :

$$\left. \begin{aligned} S_{ij}(s_1, s_2, p, \theta) &\equiv \frac{\partial}{\partial s_j} f_i(s_1, s_2, p, \theta) \\ P_i(s_1, s_2, p, \theta) &\equiv \frac{\partial}{\partial p} f_i(s_1, s_2, p, \theta) \\ f'_i(s_1, s_2, p, \theta) &\equiv \frac{\partial}{\partial \theta} f_i(s_1, s_2, p, \theta) \end{aligned} \right\} \begin{matrix} \\ (i=0, 1, 2) \\ (j=1, 2). \end{matrix}$$

This notation is convenient for many reasons, the chief of which is that the ordinary differential notation is ambiguous in cases where there is a relation between the variables. Thus if  $\Pi$  is the vapour pressure of a solution of concentrations  $s_1$  and  $s_2$  at a temperature  $\theta$ , the symbol

$$\frac{\partial}{\partial s_1} f_1(s_1, s_2, \Pi, \theta)$$

may mean either the quantity

$$\left[ \frac{\partial}{\partial s_1} f_1(s_1, s_2, p, \theta) \right]_{p=\Pi},$$

which, according to the above system of notation, is denoted by  $S_{11}(s_1, s_2, \Pi, \theta)$ , or the quantity

$$S_{11}(s_1, s_2, \Pi, \theta) + P_1(s_1, s_2, \Pi, \theta) \frac{\partial \Pi}{\partial s_1}.$$

The quantities  $P_i$  are connected with the specific volume  $v(s_1, s_2, p, \theta)$  of the mixture by the equations

$$P_0(s_1, s_2, p, \theta) = v(s_1, s_2, p, \theta) - (1 + s_1 + s_2) \left( s_1 \frac{\partial v}{\partial s_1} + s_2 \frac{\partial v}{\partial s_2} \right). \quad (21)$$

$$P_1(s_1, s_2, p, \theta) = v(s_1, s_2, p, \theta) + (1 + s_1 + s_2) \frac{\partial v}{\partial s_1}. \quad (22)$$

$$P_2(s_1, s_2, p, \theta) = v(s_1, s_2, p, \theta) + (1 + s_1 + s_2) \frac{\partial v}{\partial s_2}. \quad (23)$$

It is easily proved that  $P_i$  is the increase of volume of a large mass of the mixture when unit mass of  $C_i$  is added to it.

### 3. *The Variation of the Chemical Potentials with the Composition of the Mixture.*

In the case of a binary mixture the further addition of one of the components raises the chemical potential of that component and lowers that of the other. From inequalities (14), (15), and (16) we see that in the case of a ternary mixture the further addition of one of the components raises the chemical potential of that component. It does not follow from this, however, that this addition necessarily lowers the chemical potential of the other components.

We will examine this point a little more closely. Suppose

that the further addition of  $C_1$  raises the chemical potential of  $C_2$ , i. e. that

$$\frac{\partial F_2}{\partial M_1} > 0.$$

From equation (6) we see that

$$\frac{\partial F_1}{\partial M_2} > 0.$$

From equation (4) and inequality (15) we see that

$$\frac{\partial F_0}{\partial M_1} < 0.$$

From equation (5) and inequality (16) we see that

$$\frac{\partial F_0}{\partial M_2} < 0.$$

From equations (7) and (8) respectively we see that

$$\frac{\partial F_2}{\partial M_0} < 0,$$

and

$$\frac{\partial F_1}{\partial M_0} < 0.$$

We may therefore draw the following conclusions with respect to the variation of the chemical potentials with the composition of the mixture.

(1) The further addition of one component raises the chemical potential of that component, and may either raise or lower the potential of another component.

(2) If the further addition of a component A raises (lowers) the potential of a component B, then the further addition of B raises (lowers) the chemical potential of A.

(3) If two components thus cause, by their further addition to the mixture, a mutual raising of each other's potentials, any other two components must cause a mutual lowering.

#### 4. *Equilibrium between Liquid and Vapour Phases.*

Suppose that a liquid mixture of  $C_0$ ,  $C_1$ , and  $C_2$  is in equilibrium with a mixture of the vapours of these components. If for quantities relating to the vapour phase, we use the corresponding symbol relating to the liquid phase, with the addition of an asterisk, the equilibrium equations may be written in the form

$$f_i(s_1, s_2, \Pi, \theta) = f_i^*(s_1^*, s_2^*, \Pi, \theta) \dots (i=0, 1, 2). \quad (24)$$



These equations determine the vapour pressure  $\Pi$  and the concentrations  $s_1^*$  and  $s_2^*$  as functions of  $s_1$ ,  $s_2$ , and  $\theta$ . If we differentiate these equations with respect to  $s_1$  and  $s_2$ , we obtain six equations containing the following quantities :—

the twelve quantities,

$$\frac{\partial}{\partial s_1} \text{ and } \frac{\partial}{\partial s_2} \text{ of } \Pi, s_1^*, \text{ and } s_2^*,$$

$$\frac{\partial}{\partial p} \text{ of } f_0, f_1, f_2, f_0^*, f_1^*, f_2^*,$$

which may be determined experimentally ;  
and the twelve differential coefficients,

$$\frac{\partial f_i}{\partial s_j} \text{ and } \frac{\partial f_i^*}{\partial s_j^*} \quad (i=0, 1, 2 : j=1, 2).$$

The twelve differential coefficients are reducible to six by means of equations (9), (10), (11) and the corresponding equations relating to the vapour phase. The coefficients may therefore be evaluated in terms of the experimental magnitudes. Hence the experimental data relating to the equilibrium suffice for the complete thermodynamical study of the mixture. If one of the components is involatile, both the number of equations and the number of differential coefficients are reduced to four, so that the complete study is still possible. If, however, only one component is volatile, the complete study is not possible.

Considerable simplification is introduced if it is assumed that the mixture of vapours obeys the partial pressure law. The equilibrium equations may then be written in the form

$$f_0(s_1, s_2, \Pi, \theta) = F_0(\Pi_0, \theta) \quad . \quad . \quad . \quad (25)$$

$$f_1(s_1, s_2, \Pi, \theta) = F_1(\Pi_1, \theta) \quad . \quad . \quad . \quad (26)$$

$$f_2(s_1, s_2, \Pi, \theta) = F_2(\Pi_2, \theta), \quad . \quad . \quad . \quad (27)$$

where  $\Pi_i$  is the partial pressure and  $F_i$  the chemical potential of the vapour of  $C_i$ . If in addition we neglect the specific volumes of the liquid components in comparison with those of the vapours, we may regard the chemical potentials of the components in the liquid phase as independent of the pressure, so that we obtain by differentiation

$$S_{ij}(s_1, s_2, p, \theta) = V_i(\Pi_i, \theta) \frac{\partial \Pi_i}{\partial s_j} \quad (i=0, 1, 2 : j=1, 2), \quad (28)$$

where  $V_i$  is the specific volume of the vapour of  $C_i$ , and  $p$  is any pressure not too far removed from the vapour pressure.

From equations (9), (10), (11), and (28) we can deduce immediately the following equations

$$V_0(\Pi_0, \theta) \frac{\partial \Pi_0}{\partial s_1} + s_1 V_1(\Pi_1, \theta) \frac{\partial \Pi_1}{\partial s_1} + s_2 V_2(\Pi_2, \theta) \frac{\partial \Pi_2}{\partial s_1} = 0, \quad (29)$$

$$V_0(\Pi_0, \theta) \frac{\partial \Pi_0}{\partial s_2} + s_1 V_1(\Pi_1, \theta) \frac{\partial \Pi_1}{\partial s_2} + s_2 V_2(\Pi_2, \theta) \frac{\partial \Pi_2}{\partial s_2} = 0, \quad (30)$$

$$V_1(\Pi_1, \theta) \frac{\partial \Pi_1}{\partial s_2} = V_2(\Pi_2, \theta) \frac{\partial \Pi_2}{\partial s_1}. \quad (31)$$

If we assume that the vapours behave as ideal gases, *i. e.* that

$$\Pi_i V_i(\Pi_i, \theta) = \frac{R\theta}{m_i} \dots (i=0, 1, 2), \quad (32)$$

where  $R$  is the gas constant and  $m_i$  the molecular weight of the vapour of  $C_i$ ; and if we write

$$c_1 = \frac{s_1 m_0}{m_1}$$

$$c_2 = \frac{s_2 m_0}{m_2},$$

where  $c_1$  and  $c_2$  are the molecular concentrations of  $C_1$  and  $C_2$  respectively, then equations (29), (30), and (31) become

$$\frac{\partial \log \Pi_0}{\partial c_1} + c_1 \frac{\partial \log \Pi_1}{\partial c_1} + c_2 \frac{\partial \log \Pi_2}{\partial c_1} = 0. \quad (33)$$

$$\frac{\partial \log \Pi_0}{\partial c_2} + c_1 \frac{\partial \log \Pi_1}{\partial c_2} + c_2 \frac{\partial \log \Pi_2}{\partial c_2} = 0. \quad (34)$$

$$\frac{\partial \log \Pi_1}{\partial c_2} = \frac{\partial \log \Pi_2}{\partial c_1}. \quad (35)$$

These three equations correspond to the single Duhem-Margules equation for a binary mixture.

If the component  $C_2$  is involatile equation (30) contains an indeterminate term, and equations (29) and (31) give

$$V_0(\Pi_0, \theta) \frac{\partial \Pi_0}{\partial s_1} + s_1 V_1(\Pi_1, \theta) \frac{\partial \Pi_1}{\partial s_1} + s_2 V_1(\Pi_1, \theta) \frac{\partial \Pi_1}{\partial s_2} = 0. \quad (36)$$

Similarly equations (33), (34), and (35) reduce to

$$\frac{\partial \log \Pi_0}{\partial c_1} + c_1 \frac{\partial \log \Pi_1}{\partial c_1} + c_2 \frac{\partial \log \Pi_1}{\partial c_2} = 0. \quad (37)$$

We shall return to the consideration of vapour pressure in the next section. It may be remarked here that the three general

laws stated at the end of section 3 are true if the term "partial pressure" is substituted for "chemical potential."

### 5. Solubility Influence.

Suppose that a solid substance  $C_2$  is in equilibrium with a solution of  $C_2$  in a liquid mixture of  $C_0$  and  $C_1$ . The concentration  $s_2$  of  $C_2$  in the mixture is determined as a function of the pressure, temperature, and concentration  $s_1$  of  $C_1$ , by the equation

$$f_2(s_1, s_2, p, \theta) = \phi_2(p, \theta), \quad . \quad . \quad . \quad (38)$$

where  $\phi_2$  is the chemical potential of  $C_2$  in the pure solid state.

Differentiating equation (38) with respect to  $s_1$  we obtain the equation

$$\frac{\partial s_2}{\partial s_1} = - \frac{S_{21}(s_1, s_2, p, \theta)}{S_{22}(s_1, s_2, p, \theta)} \quad . \quad . \quad . \quad (39)$$

If we regard  $C_0$  as the solvent and  $C_1$  as an added substance whose effect on the solubility is being studied, then  $s_2$  may be termed the solubility of  $C_2$  in the binary mixture of  $C_0$  and  $C_1$ . Of course, if  $C_1$  is a liquid perfectly miscible with  $C_0$ , this mode of defining the solubility is quite an arbitrary one.

From equation (39) we see that the further addition of  $C_1$  increases or decreases the solubility of  $C_2$ , according as it lowers or raises the chemical potential of  $C_2$ . This, of course, is evident from general considerations. If, for example, the further addition of  $C_1$  raises the chemical potential of  $C_2$ , then the addition of  $C_1$  to the saturated solution will make the potential of  $C_2$  greater than that of the solid  $C_2$ , and in the presence of the latter will cause a certain amount of  $C_2$  to be precipitated.

In the following table are given the results of measurements of the solubility of cane-sugar ( $C_2$ ) in mixtures of water ( $C_0$ ) and alcohol ( $C_1$ )\*.

TABLE I.  
Temperature 14° C.

$s_1$ .	$s_2$ .
0	1.94
.087	1.82
.194	1.70
.328	1.62
.501	1.44

\* Quoted by Rothmund, *Löslichkeit und Löslichkeitsbeeinflussung*, p. 140.

We see from this table that the addition of alcohol to a solution of sugar in a mixture of alcohol and water raises the chemical potential of the sugar. Hence by equation (6) the addition of sugar must raise the chemical potential of the alcohol. Strictly speaking, equation (39) justifies these statements for solutions only in the neighbourhood of saturation. A little consideration will show, however, that the statements are probably true over a considerable range of values of the concentrations. Consider a mixture for which  $s_1=0$  and  $s_2=1.44$ . The chemical potential of sugar in the mixture will be less than that of pure sugar. If alcohol be added till  $s_1=.501$ , then the chemical potential will rise to that of pure sugar. Of course the first addition might cause the potential of sugar to fall, but it is reasonable to suppose that a rise occurs over a considerable range of values of  $s_1$ , if not from zero to .501.

In a binary mixture, the two components exert a lowering effect on each other's potentials. Hence in a ternary mixture in which one of the components forms only a very small proportion of the whole mass, the other two components must exert a lowering effect on each other's potentials. Thus in a system containing alcohol, sugar, and a very small amount of water, the further addition of alcohol must lower the chemical potential of the sugar. Hence as the numbers in the first column are increased a point must be reached when the numbers in the second column begin to increase. This of course is simple common sense. When the solvent medium is practically pure alcohol, the amount of sugar dissolved will be proportional to the amount of alcohol present. In any system of this kind, if  $s_2$  be plotted against  $s_1$  the curve is asymptotic to a straight line through the origin whose slope measures the solubility of  $C_2$  in  $C_1$ .

If the addition of  $C_1$  lowers the solubility of  $C_2$  in  $C_0$ , it raises the potential of  $C_2$ , and hence from equation (11) we see that the addition of  $C_2$  raises the potential of  $C_1$ . Hence from equation (10) we see that the addition of  $C_1$  lowers the potential of  $C_0$ . If, however, the addition of  $C_1$  raises the solubility, the addition of  $C_2$  lowers the potential of  $C_1$ , and hence from equation (10) we see that the addition of  $C_2$  may either raise or lower the potential of  $C_0$ . We will next, therefore, find the condition which must be fulfilled with respect to the solubility in order that the addition of  $C_2$  may raise the potential of  $C_0$ .

From equations (10) and (39) we can deduce the equation

$$s_1^2 \frac{\partial}{\partial s_1} \left( \frac{s_2}{s_1} \right) = \frac{S_{02}}{S_{22}} \quad \dots \quad (40)$$



Hence, if the addition of  $C_1$  raises not merely the solubility of  $C_2$ , but also the ratio of this solubility to the concentration of  $C_1$ , the addition of  $C_2$  raises the chemical potential of  $C_0$ . An example of this is afforded by the system water ( $C_0$ ), zinc chloride ( $C_1$ ), and zinc oxide ( $C_2$ )\* (except in the case of very large values of  $s_1$ ), as will be seen from Table II.

TABLE II.  
Ordinary Temperature.

100 $s_1$ .	100 $s_2$ .	$s_2/s_1$ .
8.22	.0137	.0017
23.24	.138	.0051
51.5	.604	.0117
56.9	.723	.0127
62.85	.884	.0141
96.00	1.792	.0186
144.8	2.64	.0182
203.0	1.59	.0078

We have thus three cases of solubility influence:—

- (1) Solubility Lowering: the addition of  $C_1$  to the two-phase system precipitates  $C_2$ , the addition of  $C_0$  causes more  $C_2$  to dissolve. In this case  $S_{01} < 0$ ,  $S_{02} < 0$ , and  $S_{12} > 0$ .
- (2) Solubility Raising: the addition of  $C_1$  causes more  $C_2$  to dissolve, the addition of  $C_0$  precipitates  $C_2$ . In this case  $S_{01} < 0$ ,  $S_{02} > 0$ , and  $S_{12} < 0$ .
- (3) Solubility Raising: the addition of either  $C_0$  or  $C_1$  causes more  $C_2$  to dissolve.

If  $C_0$  and  $C_1$  are perfectly miscible liquids, the distinction between cases (1) and (2) is merely an arbitrary one depending on which component is called the solvent.

The system water ( $C_0$ ), hydrochloric acid ( $C_1$ ), and lead chloride ( $C_2$ ) affords an example of each of these three cases†. For small values of  $s_1$ ,  $\partial s_2 / \partial s_1$  is negative, but becomes positive for higher values of  $s_1$ , and increases still more as  $s_1$  increases. Hence from the value  $s_1 = 0$  to the value at which  $s_2$  is a minimum, we have case (1); from this latter value to the value at which  $s_2/s_1$  is a minimum we have case (3); for still higher values of  $s_1$  we have case (2).

\* Annual Tables, vol. i. (1910), p. 399 (1912).

† Rothmund, *loc. cit.* p. 175.

If we differentiate equation (38) with respect to the pressure, we obtain the equation

$$\frac{\partial s_2}{\partial p} = \frac{v_2(p, \theta) - P_2(s_1, s_2, p, \theta)}{S_{22}(s_1, s_2, p, \theta)}, \quad \dots \quad (41)$$

where  $v_2$  is the specific volume of  $C_2$  in the solid state. When a mass  $\delta M_2$  of  $C_2$  passes from the solid to the liquid mixture in the neighbourhood of saturation the decrease of volume is  $(v_2 - P_2) \delta M_2$ . Moreover,  $S_{22}$  is always positive. Hence equation (41) is in agreement with the general principle of the displacement of equilibrium by variations of pressure\*.

Differentiating equation (38) with respect to the temperature, we obtain the equation

$$\frac{\partial s_2}{\partial \theta} = \frac{\phi_2'(p, \theta) - f_2'(s_1, s_2, p, \theta)}{S_{22}(s_1, s_2, p, \theta)}, \quad \dots \quad (42)$$

where  $\phi_2' \equiv \partial \phi_2 / \partial \theta$ . If now  $l_2(s_1, s_2, p, \theta)$  denote the heat of solution of  $C_2$  in the saturated liquid mixture (heat evolved) we have †

$$\theta(f_2' - \phi_2') = l_2(s_1, s_2, p, \theta).$$

Hence we have

$$\frac{\partial s_2}{\partial \theta} = - \frac{l_2(s_1, s_2, p, \theta)}{\theta S_{22}(s_1, s_2, p, \theta)}. \quad \dots \quad (43)$$

It will readily be seen that this equation is in agreement with the general principle of the displacement of equilibrium by variations of temperature ‡.

From equations (41) and (43) we obtain

$$\frac{\frac{\partial s_2}{\partial \theta}}{\frac{\partial s_2}{\partial p}} = - \frac{l_2(s_1, s_2, p, \theta)}{\theta \{v_2(p, \theta) - P_2(s_1, s_2, p, \theta)\}} \quad \dots \quad (44)$$

Hence if simultaneous increments  $\delta p$  and  $\delta \theta$  of the pressure and temperature respectively, cause no change in the solubility, we have

$$\frac{\delta p}{\delta \theta} = \frac{l_2(s_1, s_2, p, \theta)}{\theta \{v_2(p, \theta) - P_2(s_1, s_2, p, \theta)\}} \quad \dots \quad (45)$$

An equation similar to this, applicable to a binary solution,

\* Duhem, *La Mécanique Chimique*, vol. i. p. 145.

† Duhem, *loc. cit.* vol. iii. p. 127.

‡ Duhem, *loc. cit.* vol. i. p. 184.

has been obtained previously and tested experimentally \*. A similar equation will evidently apply to the case of a single solid component in equilibrium with a solution in a solvent medium containing any number of components.

We will now consider the relation between solubility influence and vapour pressure. Let us first assume that  $C_0$  and  $C_1$  are volatile and  $C_2$  is involatile—a case often occurring in practice. We will assume that the binary vapour mixture obeys the partial pressure law. From equations (39), (10), and (28) we obtain the relation

$$\frac{1}{s_2} \frac{\partial s_2}{\partial s_1} = \left[ \frac{V_1(\Pi_1, \theta) \frac{\partial \Pi_1}{\partial s_2}}{V_0(\Pi_0, \theta) \frac{\partial \Pi_0}{\partial s_2} + s_1 V_1(\Pi_1, \theta) \frac{\partial \Pi_1}{\partial s_2}} \right]_{s_2=s_2} \quad (46)$$

If we assume that the vapours obey the ideal gas laws, and if we introduce the molecular concentrations, the above equation reduces to

$$\frac{1}{c_2} \frac{\partial c_2}{\partial c_1} = \left[ \frac{\frac{\partial \log \Pi_1}{\partial c_2}}{\frac{\partial \log \Pi_0}{\partial c_2} + c_1 \frac{\partial \log \Pi_1}{\partial c_2}} \right]_{c_2=c_2} \quad (47)$$

where  $c_2$  is the molecular saturation concentration.

There are no experimental data available for the quantitative verification of the above theory. The theory is verified qualitatively, however, by the experiments of Kablukow, Solomonow, and Galine †, who have investigated the effect of the addition of various salts on the pressure and composition of the vapour of mixtures of alcohol and water. These investigators find that the partial pressure of the alcohol is raised by the addition of potassium chloride, bromide, and iodide, but lowered by the addition of mercurous chloride. Now the addition of alcohol raises the solubility of the last of these salts, but lowers the solubilities of the others. These facts are, of course, in agreement with the above theory ‡.

If only the component  $C_0$  is volatile, we can deduce only qualitative relationships between solubility influence and vapour pressure. If the addition of  $C_1$  lowers the solubility

\* See Duhem, *loc. cit.* vol. iii. p. 129; Braun, Wied. *Ann.* xxx. p. 250 (1887); von Stackelberg, *Zeit. für Phys. Chem.* xx. p. 337 (1896).

† *Zeitsch. für Phys. Chem.* xlv. p. 399 (1903).

‡ This qualitative relationship, which is perhaps not readily apparent from equation (47), is easily deduced from general considerations or from equations (28) and (39).

of  $C_2$ , then the addition of  $C_2$  to a mixture in the neighbourhood of saturation lowers the vapour pressure. If the addition of  $C_1$  raises the solubility but not the value of the ratio  $s_2/s_1$ , the addition of  $C_2$  lowers the vapour pressure. If the addition of  $C_1$  raises the value of the ratio  $s_2/s_1$ , the addition of  $C_2$  raises the vapour pressure. Thus in the case of a moderately concentrated aqueous solution of zinc chloride nearly saturated with zinc oxide, the addition of zinc oxide will raise the vapour pressure of the mixture. In the case of a similar mixture containing a very large proportion of zinc chloride, the addition of zinc oxide will lower the vapour pressure\*.

### 6. *Osmotic Equilibrium.*

There are two distinct cases of osmotic equilibrium, one in which the membrane is permeable to two of the components, the other in which the membrane is permeable to one component only. We will deal with the former case only very briefly.

#### Case I. *The membrane permeable to two components.*

Suppose that we have a mixture of  $C_0$  and  $C_1$  and a mixture of  $C_0$ ,  $C_1$ , and  $C_2$  in equilibrium on opposite sides of a membrane permeable to  $C_0$  and  $C_1$ . For equilibrium it is necessary that the potentials of  $C_0$  and  $C_1$  shall have respectively the same values on both sides of the membrane. It is evident that a mere increase of pressure will not in general bring about this double equality, and that a further adjustment is necessary, viz. a difference in the relative proportions of  $C_0$  and  $C_1$  on the two sides of the membrane. Thus equilibrium is brought about by an osmotic difference of pressure and an osmotic difference of composition of the binary solvent mixture.

This case of equilibrium differs from all the other cases discussed in the present paper in being conditioned by two equations. Any adequate treatment of it would necessarily be somewhat lengthy. We will, therefore, not discuss this case any further.

#### Case II. *The membrane permeable to one component only.*

To make the discussion as general as possible, we will assume that the membrane is permeable to the component  $C_i$  only. Suppose that  $C_i$  in the pure state under a pressure  $p_0$  is in osmotic equilibrium with the mixture under a pressure  $p$ .

\* See Table II.



The equilibrium equation is

$$\phi_i(p_0, \theta) = f_i(s_1, s_2, p, \theta), \quad . \quad . \quad . \quad (48)$$

where  $\phi_i$  is the chemical potential of  $C_i$  in the pure state. We may regard this equation as determining the osmotic difference of pressure  $p - p_0$  as a function of  $s_1, s_2, p_0$ , and  $\theta$ . If we write

$$p - p_0 = \Omega_i(s_1, s_2, p_0, \theta),$$

we have

$$\phi_i(p_0, \theta) = f_i(s_1, s_2, p_0 + \Omega_i, \theta). \quad . \quad . \quad . \quad (49)$$

By differentiation we obtain the equations

$$S_{ij}(s_1, s_2, p_0 + \Omega_i, \theta) = -P_i(s_1, s_2, p_0 + \Omega_i, \theta) \frac{\partial}{\partial s_j} \Omega_i(s_1, s_2, p_0, \theta) \\ \dots (i=0, 1, 2; j=1, 2). \quad . \quad . \quad (50)$$

From these equations we see that the addition to the mixture of the component to which the membrane is permeable always lowers the osmotic pressure, but that the addition of one of the other components may either raise or lower the osmotic pressure. If the addition of one of these latter components lowers the osmotic pressure, the addition of the other must raise it.

By the use of one kind of membrane, only two of the quantities  $S_{ij}$  may be evaluated. The use of the three membranes gives the value of all six of these quantities. Since these six are connected by the three equations (9), (10), and (11), we have the following relations between the different osmotic pressures :

$$P_0 \frac{\partial \Omega_0}{\partial s_1} + s_1 P_1 \frac{\partial \Omega_1}{\partial s_1} + s_2 P_2 \frac{\partial \Omega_2}{\partial s_1} = 0 \quad . \quad . \quad . \quad (51)$$

$$P_0 \frac{\partial \Omega_0}{\partial s_2} + s_1 P_1 \frac{\partial \Omega_1}{\partial s_2} + s_2 P_2 \frac{\partial \Omega_2}{\partial s_2} = 0 \quad . \quad . \quad . \quad (52)$$

$$P_1 \frac{\partial \Omega_1}{\partial s_2} = P_2 \frac{\partial \Omega_2}{\partial s_1}. \quad . \quad . \quad (53)$$

Equation (48) may be regarded as determining  $p - p_0$  as a function of  $s_1, s_2, p$ , and  $\theta$ . If we write

$$p - p_0 = \Gamma_i(s_1, s_2, p, \theta),$$

we have

$$\phi_i(p - \Gamma_i, \theta) = f_i(s_1, s_2, p, \theta),$$

so that

$$S_{ij}(s_1, s_2, p, \theta) = -v_i(p - \Omega_i, \theta) \frac{\partial}{\partial s} \Gamma_i(s_1, s_2, p, \theta), \quad (54)$$

where  $v_i$  is the specific volume of  $C_i$  in the pure state. From equations (9), (10), (11), and (54) we can readily deduce the following relations between the different osmotic pressures:

$$v_0 \frac{\partial \Gamma_0}{\partial s_1} + s_1 v_1 \frac{\partial \Gamma_1}{\partial s_1} + s_2 v_2 \frac{\partial \Gamma_2}{\partial s_1} = 0. \quad . \quad . \quad . \quad (55)$$

$$v_0 \frac{\partial \Gamma_0}{\partial s_2} + s_1 v_1 \frac{\partial \Gamma_1}{\partial s_2} + s_2 v_2 \frac{\partial \Gamma_2}{\partial s_2} = 0. \quad . \quad . \quad . \quad (56)$$

$$v_1 \frac{\partial \Gamma_1}{\partial s_2} = v_2 \frac{\partial \Gamma_2}{\partial s_1} \quad . \quad . \quad . \quad (57)$$

We will next consider the connexion between osmotic equilibrium and vapour pressure.

We will first deduce a few qualitative relationships from general considerations. Consider the system water ( $C_0$ ), alcohol ( $C_1$ ), and potassium chloride ( $C_2$ ). The further addition of potassium chloride raises the partial pressure of the alcohol\*. Suppose now that the ternary mixture is separated from pure alcohol by a membrane permeable to alcohol, equilibrium being maintained by a suitable osmotic difference of pressure. The further addition of potassium chloride will raise the chemical potential of the alcohol, so that if the pressures are kept constant, alcohol will pass from the mixture to the pure alcohol. To prevent this the original osmotic difference of pressure would have to be diminished.

Speaking generally, we may say that if the further addition of  $C_2$  raises (lowers) the partial pressure of  $C_1$ , it lowers (raises) what may be termed the osmotic pressure of  $C_0$  and  $C_2$  in the solvent medium  $C_1$ . If the addition of  $C_2$  lowers the osmotic pressure, the addition of  $C_0$  must raise it.

Quantitative relationships between osmotic pressure and vapour pressure may be obtained from equations (28) and (54). Thus we have the equations

$$v_1 \frac{\partial \Gamma_1}{\partial s_1} = -V_1 \frac{\partial \Pi_1}{\partial s_1}. \quad . \quad . \quad . \quad (58)$$

$$v_1 \frac{\partial \Gamma_1}{\partial s_2} = -V_1 \frac{\partial \Pi_1}{\partial s_2}, \quad . \quad . \quad . \quad (59)$$

connecting the osmotic pressure with the partial pressure of the component to which the membrane is permeable.

Equations connecting the osmotic pressure with the partial pressures of the components to which the membrane is impermeable may be obtained from the above equations by

\* Kablukow, Solomonow, and Galine, *loc. cit.*

means of equations (29) and (30). We have

$$s_1 v_1 \frac{\partial F_1}{\partial s_1} = V_0 \frac{\partial \Pi_0}{\partial s_1} + s_2 V_2 \frac{\partial \Pi_2}{\partial s_1}, \quad \dots \quad (60)$$

and

$$s_1 v_1 \frac{\partial F_1}{\partial s_2} = V_0 \frac{\partial \Pi_0}{\partial s_2} + s_2 V_2 \frac{\partial \Pi_2}{\partial s_2}. \quad \dots \quad (61)$$

These equations and also equations (58) and (59) may be simplified if we assume that the vapour phase forms an ideal gaseous mixture and introduce the molecular concentrations.

We will now consider the relation between osmotic equilibrium and solubility influence. It is evident from general considerations that if the addition of  $C_1$  raises (lowers) the solubility of  $C_2$  in  $C_0$ , the addition of  $C_2$  to a mixture in the neighbourhood of saturation raises (lowers) the osmotic pressure measured by a membrane permeable to  $C_1$ . If the addition of  $C_1$  raises (lowers) the ratios of the saturation concentration of  $C_2$  to the concentration of  $C_1$ , then the addition of  $C_2$  lowers (raises) the osmotic pressure of  $C_1$  and  $C_2$  in the solvent medium  $C_0$  (*i. e.* the osmotic pressure measured by a membrane permeable to  $C_0$ ). Thus if to a solution of zinc chloride ( $C_1$ ) and zinc oxide ( $C_2$ ) in water ( $C_0$ ) of composition, say,  $s_1 = \cdot 24$ ,  $s_2 = \cdot 0014$  †, a small amount of zinc oxide be added, the osmotic pressure of the zinc oxide and zinc chloride in the water is decreased. If, however, a small amount of zinc oxide be added to a solution of composition, say,  $s_1 = 2\cdot 0$ ,  $s_2 = \cdot 015$  †, the osmotic pressure is increased.

### 7. Partition Equilibrium.

We will first consider the two-phase liquid system formed by two immiscible liquids  $C_0$  and  $C_0^*$ , and two substances  $C_1$  and  $C_2$ ,  $C_1$  being soluble in  $C_0$  only, and  $C_2$  being soluble in both liquids.

If  $s_2^*$  denote the concentration and  $f_2^*$  ( $s_2^*$ ,  $p$ ,  $\theta$ ) the chemical potential of  $C_2$  in the  $C_0^*$  phase, the equilibrium equation may be written in the form

$$f_2(s_1, s_2, p, \theta) = f_2^*(s_2^*, p, \theta). \quad \dots \quad (62)$$

We may regard this equation as determining  $s_2^*$  as a function of  $s_1$ ,  $s_2$ ,  $p$ , and  $\theta$ . By differentiation we obtain the equations

$$S_{21}(s_1, s_2, p, \theta) = S_2^*(s_2^*, p, \theta) \frac{\partial s_2^*}{\partial s_1}, \quad \dots \quad (63)$$

$$S_{22}(s_1, s_2, p, \theta) = S_2^*(s_2^*, p, \theta) \frac{\partial s_2^*}{\partial s_2}, \quad \dots \quad (64)$$

where  $S_2^* \equiv \partial f_2^* / \partial s_2^*$ .

† See Table II.

From equation (64) we see that the addition of  $C_2$  to the  $C_0$  phase always causes an increase of the concentration of  $C_2$  in the  $C_0^*$  phase. From equation (63) we see that the addition of  $C_1$  may cause either an increase or a decrease of the concentration of  $C_2$  in the  $C_0^*$  phase.

The quantity  $S_2^*$  may be evaluated from a knowledge of the thermodynamical properties of the solution of  $C_2$  in  $C_0^*$  by means of formulæ which I have given previously †. Hence the quantities  $S_{12}$  and  $S_{22}$  may be evaluated from partition equilibrium data and data relating to the solution of  $C_2$  in  $C_0^*$ .

If we regard equation (62) as determining  $s_2$  as a function of  $s_1$ ,  $s_2^*$ ,  $p$ , and  $\theta$ , we have the equation

$$\frac{\partial s_2}{\partial s_1} = - \frac{S_{21}(s_1, s_2, p, \theta)}{S_{22}(s_1, s_2, p, \theta)}, \quad \dots \quad (65)$$

which does not involve the properties of the solution of  $C_2$  in  $C_0^*$ . It will be seen that this equation is very similar to equation (39) in the section dealing with Solubility Influence. This similarity is due to the similarity of the corresponding experimental processes. In both cases we are investigating the manner in which  $s_1$  and  $s_2$  must vary simultaneously so as to keep the potential of  $C_2$  constant, —in one case equal to the potential of solid  $C_2$  and in the other equal to that of  $C_2$  in a solution of  $C_2$  in  $C_0^*$  of a certain concentration.

We will next consider another two-phase liquid system. Suppose that  $C_0$  and  $C_1$  are two slightly miscible liquids, and that  $C_2$  is a substance soluble in  $C_0$ , but insoluble in  $C_1$ . The two-phase liquid system formed by these substances will consist of a ternary mixture of  $C_0$ ,  $C_1$ , and  $C_2$ , and (if we neglect the very small amount of  $C_2$  dissolved in the  $C_1$  phase owing to the presence of  $C_0$ ) a binary mixture of  $C_1$  and  $C_0$ . The effect of variations of pressure on such a system has been investigated by Trouton ‡, the components being water ( $C_0$ ), ether ( $C_1$ ), and sugar ( $C_2$ ). As the theoretical treatment by Trouton of his experimental results is erroneous, we will consider the correct theory of the experiment.

When ether is placed in contact with water, a certain amount of water is absorbed by unit mass of ether. If ether is placed in contact with an aqueous solution of sugar, less water is absorbed by the ether. Trouton finds that if the pressure on this latter system is increased more water is absorbed by the ether, and that at a certain pressure the

† Phil. Mag. xxv. p. 31 (1913).

‡ Roy. Soc. Proc. lxxxvi. A. p. 149 (1912).



composition of the ether phase is the same as that of the ether phase in equilibrium with water at atmospheric pressure. According to Trouton, the increase of pressure necessary to bring about this equality of concentration is the osmotic pressure of the sugar solution.

This statement necessarily involves the assumption that the effect of the ether dissolved in the water phase is negligible. If we make this assumption, the correct theory of the experiment is quite simple. Let  $\lambda$  represent the increase of volume of a large mass of sugar solution when unit mass of water is added to it, and  $\mu$  the corresponding quantity in the case of the ethereal solution of water. Consider pure water and the sugar solution under atmospheric pressure. The chemical potential of the water in the sugar solution will be less than that of the pure water. Now suppose that if the pressure on the solution is increased by an amount  $\Omega$ , the two potentials are equalized.  $\Omega$  will, of course, be equal to the osmotic pressure of the sugar solution. If we neglect the variation of  $\lambda$  with the pressure, this increase of pressure will cause an increase  $\Omega\lambda$  of the potential of the water in the sugar solution. This quantity is therefore equal to the original difference in the potentials of the water. Now consider the sugar solution and an ethereal solution of water of the same composition as that which was in equilibrium with water under atmospheric pressure. Suppose that these two solutions are separate and under atmospheric pressure. The potential of the water in the sugar solution will be less than that in the ethereal solution by an amount  $\Omega\lambda$ . Now suppose that the pressures on the two solutions are increased at the same rate till the potential of the water has the same value in both systems. The potential difference will evidently diminish at the rate  $\lambda - \mu$  per unit of pressure, so that if  $P$  is the increase of pressure necessary to bring about this equality we have

$$P(\lambda - \mu) = \Omega\lambda. \quad . \quad . \quad . \quad . \quad . \quad (66)$$

Now  $\lambda$  and  $\mu$  will both be roughly equal to the specific volume of pure water. Hence the ratio  $P/\Omega$  will have a very high positive or negative value\*. Trouton's theoretical deduction that this ratio has the value unity is therefore quite erroneous. The verification of this deduction in one

\* In general the increase of volume of a liquid system, due to the further addition of a liquid component, is slightly less than the volume of the liquid added, but becomes more nearly equal to it the greater the amount of the component in the system. In general, therefore, we have  $\lambda > \mu$ , so that  $P/\Omega$  is positive.

special case is, of course, a mere coincidence. The fact that in the experiment P is not found to be much greater than  $\Omega$  simply demonstrates the incorrectness of the initial assumption that the effect of the ether dissolved in the water phase is negligible\*.

### 8. *The Freezing of Ternary Mixtures.*

Suppose that we have a solution of two substances  $C_1$  and  $C_2$  in a liquid  $C_0$ , and that  $C_0$  in the solid state is in equilibrium with the solution at a temperature  $T$ , and with  $C_0$  in the pure liquid state at a temperature  $T_0$ .

The equation

$$f_0(s_1, s_2, p, T) = \psi_0(p, T), \quad . \quad . \quad . \quad (67)$$

where  $\psi_0$  is the chemical potential of  $C_0$  in the solid state, determines  $T$  as a function of  $s_1$ ,  $s_2$ , and  $v$ .

The equation

$$\phi_0(p, T_0) = \psi_0(p, T_0), \quad . \quad . \quad . \quad (68)$$

where  $\phi_0$  is the chemical potential of  $C_0$  in the liquid state, determines  $T_0$  as a function of  $p$ .

If  $C_0$  is the only volatile component, the theory of the relation between the vapour pressure and the freezing-point is a particular case of a more general theory which I have developed in a previous work†. The same is true of the theory of the relation between the freezing-point and the osmotic pressure, if the latter is measured by means of a membrane permeable to  $C_0$  only.

In the above work I have given formulæ by means of which the difference (at any temperature) between the chemical potentials of  $C_0$  in the pure liquid state and in the solution, can be calculated from the freezing-point. The exact expression for this difference is rather complicated. If we suppose that  $l_0$ , the heat of dilution, and  $\gamma$ , the difference between the specific heats of  $C_0$  in the liquid and solid states, are independent of the temperature, the expression reduces to the simpler form

$$\begin{aligned} \phi_0(p, \theta) - f_0(s_1, s_2, p, \theta) = & L_0 \theta \left( \frac{1}{T} - \frac{1}{T_0} \right) - \frac{\theta - T}{T} l_0 \\ & - \gamma \theta \left( \frac{T_0 - T}{\theta} - \log \frac{T_0}{T} \right), \quad . \quad . \quad (69) \end{aligned}$$

where  $\theta$  is any temperature, and  $L_0$  is the latent heat of fusion of solid  $C_0$ .

\* A further investigation, treating the water phase as a ternary mixture, shows that this assumption is valid only if the coefficient  $S_{01}$  is negligible in comparison with  $S_{11}$ .

† Phil. Mag. vol. xxv. p. 38, Jan. 1913.

By differentiation we obtain the equations

$$S_{01}(s_1, s_2, p, \theta) = \frac{\theta}{T^2} \frac{\partial T}{\partial s_1} [L_0 - l_0 - \gamma(T_0 - T)] + \frac{\theta - T}{T} \frac{\partial l_0}{\partial s_1},$$

. . . . (70)

$$S_{02}(s_1, s_2, p, \theta) = \frac{\theta}{T^2} \frac{\partial T}{\partial s_2} [L_0 - l_0 - \gamma(T_0 - T)] + \frac{\theta - T}{T} \frac{\partial l_0}{\partial s_2}.$$

. . . . (71)

In the case of a dilute solution these equations reduce to

$$S_{01}(s_1, s_2, p, \theta) = \frac{\theta L_0}{T^2} \frac{\partial T}{\partial s_1}, \quad . . . . (72)$$

and

$$S_{02}(s_1, s_2, p, \theta) = \frac{\theta L_0}{T^2} \frac{\partial T}{\partial s_2}. \quad . . . . (73)$$

The distinction between this equilibrium and that studied under the heading "Solubility Influence" is arbitrary from a theoretical standpoint, though practically it is very convenient. If for the moment we call the component which freezes out  $C_2$ , we may apply equation (43). Since the heat of solution (*i. e.* heat of fusion) is negative in all cases which come under the head of "freezing," we see that the dilution of the mixture with the component which freezes out raises the freezing-point, and that therefore the simultaneous addition of the other components in the proportion in which they exist in the mixture, lowers the freezing-point.

The addition of one component may of course raise the freezing-point. Reverting to the original assumption that  $C_0$  is the component which freezes out, we see that the further addition of  $C_j$  raises or lowers the freezing-point according as  $S_{0j}$  is positive or negative.

The complete thermodynamical study of a ternary mixture is not possible by means of freezing-point experiments since only the two coefficients  $S_{01}$  and  $S_{02}$  can be evaluated. Thus it is impossible to connect quantitatively freezing-point and solubility data. We may, however, deduce a qualitative relationship. It is evident from general considerations, that if the further addition of  $C_0$  to a liquid mixture of  $C_0$ ,  $C_1$ , and  $C_2$  in equilibrium with solid  $C_2$ , precipitates  $C_2$  (causes more  $C_2$  to dissolve), then the addition of  $C_2$  to a solution not too far removed from saturation raises (lowers) the freezing-point.

Quantitative relationships between partial pressure and freezing-point data may readily be obtained from equations (28), (70), and (71). Thus we have

$$\frac{\theta}{T^2} \frac{\partial T}{\partial s_i} \left[ L_0 - l_0 - \gamma(T_0 - T) \right] + \frac{\theta - T}{T} \frac{\partial l_0}{\partial s_i} = V_1(\Pi_0, \theta) \frac{\partial \Pi_0}{\partial s_i} \dots (i=1, 2). \quad (74)$$

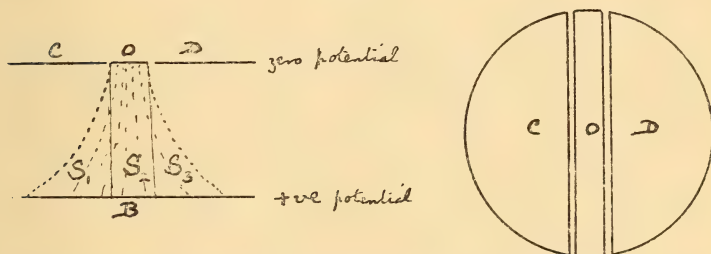
The University, Leeds,  
Sept. 18, 1913.

### CIII. Initial Stages of Ionization by Collision.

By S. SMITH, B.A., Exeter College, Oxford\*.

WHEN negative ions are liberated from a narrow electrode such as O (fig. 1), and made to move in the electronic state under the influence of a uniform electric field

Fig. 1.



between parallel-plate electrodes to B, there is found to be a considerable spreading of the beam. The amount of this spreading depends on the ratio of the applied electric force,  $Z$ , to a quantity  $k$ ,  $k$  being the ratio of the partial pressure of the ions to that of an equal number of molecules of the surrounding gas†. When the ratio of the electric force  $Z$  to the pressure  $p$  of the gas becomes sufficiently large, the negative ions produce ions in the gas by collisions. The positive ions thus produced possess at least atomic masses: their lateral diffusion may therefore be neglected, since  $Z$  is large. Hence all the positive ions produced in the spaces  $S_1$ ,  $S_2$ , and  $S_3$  reach the portions C, O, and D, respectively, of the top electrode; O being separated from C and D by very narrow spaces. It is assumed that  $\frac{Z}{p}$  is so small that the positive ions do not produce any ions by collisions. The

\* Communicated by Prof. J. S. Townsend, F.R.S.

† Prof. Townsend, Proc. Roy. Soc. A. vol. lxxxi. (1908).



positive charges which arrive at C, O, and D are therefore proportional to the number of molecules ionized by negative ions in the spaces  $S_1$ ,  $S_2$ , and  $S_3$  respectively. It is clear that with an apparatus designed on these principles one could detect the first indications of the production of ions by collisions for small values of  $\frac{Z}{p}$ .

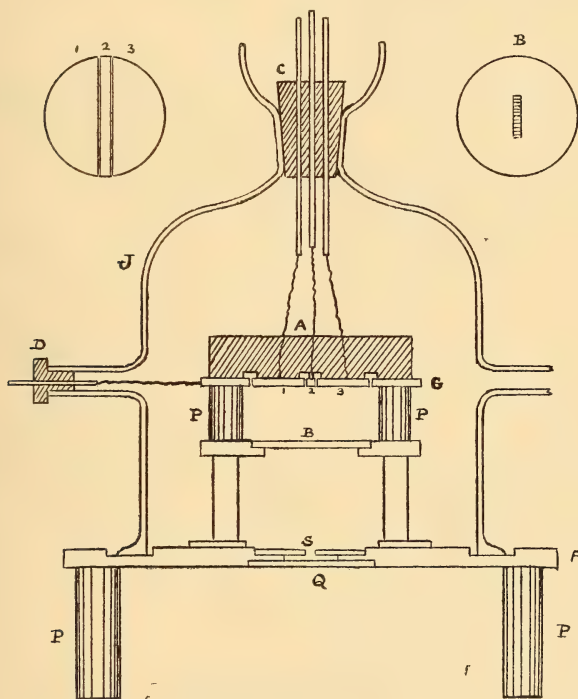
The ratio,  $\mu$ , of the number of negative ions produced by collisions in  $S_2$  to the total number produced by collisions can be found theoretically for the different values of  $\frac{Z}{p}$ . It will be seen that for the larger values of  $\alpha$  ( $\alpha$  being the number of negative ions produced by collision by a negative ion whilst moving through a distance of one centimetre in the direction of the electric field) the ratio  $\mu$  is a function of  $\alpha$ , but for the smaller values of  $\alpha$ ,  $\mu$  is independent of  $\alpha$ . The latter is the more important case, for by substituting the theoretical value of  $\mu$  in expressions found from experimental measurements values of  $\alpha$  can be deduced.

In the experiments the stream of negative ions was obtained by allowing ultra-violet light to fall on the electrode O, and as it was of great importance that the ions should be given off uniformly over the electrode, a preliminary experiment was made on the silver plate used in the apparatus. The plate and a sheet of copper gauze were used as parallel electrodes, and a narrow beam of ultra-violet light was allowed to fall on different parts of the plate. The saturation currents between the electrodes were found to be very approximately the same in every case, showing that the photoelectric effect was uniform over the plate.

The top electrodes 1, 2, and 3 (fig. 2) were cut from this plate, which was 4.5 cm. in diameter. The width of electrode 2 is 4 mm., and electrodes 1 and 3 are separated from electrode 2 by gaps of  $\frac{1}{2}$  mm. each. The bottom electrode, B, which is situated 2 cm. from electrodes 1, 2, and 3 and parallel to them, is a silvered quartz plate on which is ruled a grating of length 15 mm. and width 3 mm., the lines of the grating being equally spaced at distances of  $\frac{1}{2}$  mm. B fits into a brass ring, which is supported by brass pillars fixed to the base F. When B is in position the grating is parallel to electrode 2. G is a brass guard-ring. The pillars P, P, the block A, and the plugs C and D are all of ebonite. In the brass base is a rectangular gap, S, of length 1.5 cm. and width 3 mm. parallel to electrode 2, and the apparatus was so made that the line of centres of electrode 2, of the grating, and of the gap is normal to the

planes of the electrodes. B is a quartz plate of diameter 4.5 cm. The bell-jar, J, was so affixed as to render the apparatus air-tight. J was attached to drying-tubes, a Toepler pump, a MacLeod gauge, a pressure adjustor, and a reservoir containing a drying agent.

Fig. 2.



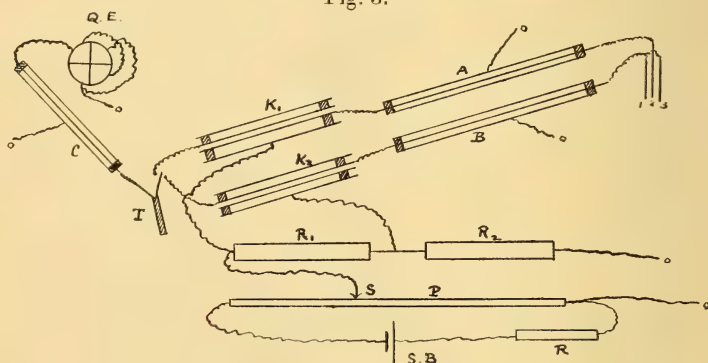
The apparatus was made in the laboratory by Mr. Bush, to whom I should like to take this opportunity of expressing my indebtedness for the accuracy shown in the construction.

The ultra-violet light was obtained from an aluminium spark-gap of length 3.5 mm. placed 6 cm. vertically below the centre of G, the length of the spark-gap being at right angles to the length of electrode 2. The Ruhmkorff coil and spark-gap were enclosed in an earthed lead box with a suitable aperture above the spark-gap.

Let  $q_0$  be the positive charge left on electrode 2 due to the liberation of negative ions by the ultra-violet light, and let  $q_1$ ,  $q_2$ , and  $q_3$  be the positive charges which arrive at electrodes 1, 2, and 3 respectively, as a result of the ionization

by collisions in the spaces  $S_1$ ,  $S_2$ , and  $S_3$ . The total charge on 2 is  $q_0 + q_2$ . The terminals of electrodes 1 and 3 were joined, and  $\frac{q_1 + q_3}{q_0 + q_2}$  was measured experimentally. For this purpose the method which is in common use in the laboratory for measuring the ratio of two charges was adopted. The arrangement is shown in fig. 3.

Fig. 3.



A, B, and C are earthed cylindrical tubes, fitted with ebonite plugs, to guard the leading wires from induction effects.  $K_1$  and  $K_2$  are cylindrical condensers of equal capacity, C. Q.E. is a Dolezalek electrometer, T a key enabling the electrometer to be put into connexion with the inside cylinder of either  $K_1$  or  $K_2$ .  $R_1$ ,  $R_2$ , and  $R$  are resistance-boxes, P a potentiometer, and S.B. a storage-battery.

The positive charge gained by the electrode 2 tends to increase the potential of the inside cylinder of condenser  $K_1$ , and this can be neutralized by bringing the outside cylinder to a certain negative potential  $V$ .

Then

$$q_0 + q_2 = -V.C.$$

Also, by adjusting the ratio of the resistance  $R_1$  to the resistance  $R_2$ , the inside cylinder of condenser  $K_2$  can at the same time be kept at zero potential. The outer cylinder of  $K_2$  is thus raised to potential  $\frac{R_2}{R_1 + R_2} \cdot V$ ;

hence

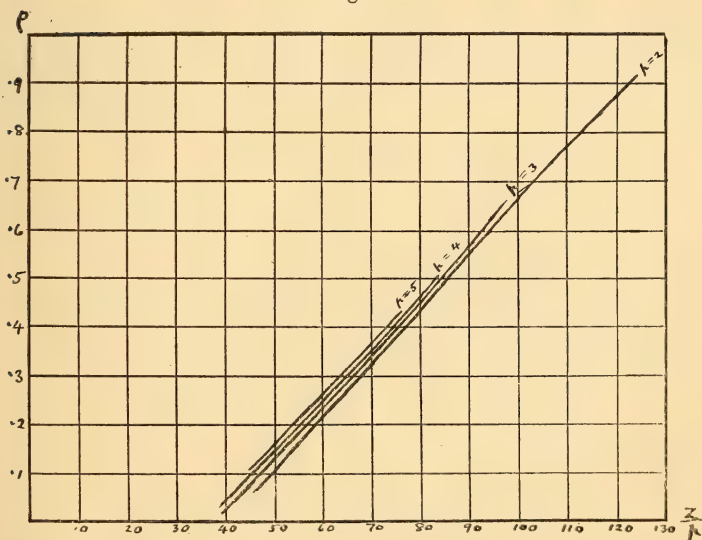
$$q_1 + q_3 = -\frac{R_2}{R_1 + R_2} \cdot V,$$

$$\therefore \frac{q_1 + q_3}{q_0 + q_2} = \frac{R_2}{R_1 + R_2} = \rho.$$

In order to obtain a measurement of  $\rho$  the electrodes 1, 2, and 3 were earthed, and the lower plate was connected to the battery. The earth connexion was then removed and the electrometer was put into connexion with the inside cylinder of  $K_1$ . The ultra-violet light was turned on for a period of time depending on the magnitude of  $\alpha$ , and the slider  $S$  was moved until the electrometer needle was brought back to its zero position. This could be done with great accuracy by using the adjustable resistance  $R$ . The electrometer was then switched on to the inside cylinder of  $K_2$ , and  $R_1$  and  $R_2$  were adjusted so that the electrometer needle was again brought to the zero position. The ratio  $\frac{R_2}{R_1 + R_2}$  was taken as a first approximation, and several more readings were taken to obtain an exact value.

The curves in fig. 4 represent the results of the experiments

Fig. 4.



made with air at pressures of 2, 3, 4, and 5 mm. of mercury. The air was dried very thoroughly by allowing it to remain in the reservoir for some weeks.

The theory requires that the rays should fall symmetrically on the electrode 2. In order to obtain this condition of symmetry the leads from electrodes 1 and 3 were connected with the inside cylinders of  $K_1$  and  $K_2$  respectively, electrode 2 was earthed, and the apparatus was moved (the slightest motion was found to be sufficient) relative to the spark-gap



to such a position that the charges gathered on electrodes 1 and 3 were equal when the light had been turned on.

In order to obtain an expression for the distribution of negative ions between the electrodes, let the geometrical centre of the face of electrode 2 be taken as the origin of rectangular coordinates, the normal to the face as the axis of  $z$ , and the axis of  $y$  parallel to the length of the electrode. Let  $n$  be the number of negative ions per cubic centimetre in the neighbourhood of the point  $(x, y, z)$ ,  $Z$  the electric force at that point in electrostatic units, and  $e$  the charge on an ion in electrostatic units. The number of ions crossing per second unit area normal to  $Z$ , may be represented as  $nw$ , and is due to the processes of diffusion and motion under the electric force, so that  $nw$  is given by the equation

$$nw = -K \frac{\partial n}{\partial z} + nw_1 Z,$$

where  $w_1$  is the mobility of the ions or velocity under unit electric force\*. This expression holds good as long as the velocity due to the electric force is small compared with  $V$ , the mean velocity of agitation. Reference to a paper by Prof. Townsend and H. T. Tizard† will show that this condition has not been violated throughout the experiments.

The velocity of the ions is therefore

$$(u, v, w) \equiv \left( -\frac{1}{n} K \frac{\partial n}{\partial x}, \quad -\frac{1}{n} K \frac{\partial n}{\partial y}, \quad -\frac{1}{n} K \frac{\partial n}{\partial z} + w_1 Z \right).$$

Taking a parallelopiped of sides  $\delta x$ ,  $\delta y$ , and  $\delta z$  about the point  $(x, y, z)$ , it is clear that the excess of the number of negative ions coming into the parallelopiped per second over those going out per second is given by

$$\Sigma \left\{ nu \delta y \delta z - \left[ nu + \frac{\partial}{\partial x} (nu) \delta x \right] \delta y \delta z \right\},$$

and this is easily seen to be

$$\left\{ K \nabla^2 (n) - w_1 Z \frac{\partial n}{\partial z} \right\} \delta x \cdot \delta y \cdot \delta z \dots \dots (1)$$

Now the number of negative ions produced per second by collisions in the parallelopiped is  $nw_1 Z \delta y \cdot \delta z \cdot \alpha \delta x$ . In the steady state the sum of these expressions must be zero, so that

$$K \cdot \nabla^2 (n) - w_1 Z \frac{\partial n}{\partial z} + n \alpha w_1 Z = 0.$$

\* Prof. Townsend, Proc. Roy. Soc. A. vol. lxxxvi. (1912).

† Proc. Roy. Soc. A. vol. lxxxviii. (1913).

But  $\frac{w_1}{K} = \frac{Ne}{k\Pi}$  \*, where  $N$  is the number of molecules per cubic centimetre in the gas at atmospheric pressure  $\Pi$  and at the temperature of the room, and  $k$  is the factor by which the energy of agitation of an electron exceeds that of a molecule of the gas,  $k$  being a function of  $\frac{Z}{p}$ . Hence (1) becomes

$$\nabla^2(n) - \gamma \frac{\partial n}{\partial z} + \gamma \cdot \alpha \cdot n = 0, \quad . \quad . \quad . \quad (2)$$

where

$$\gamma = \frac{NeZ}{k\Pi}.$$

The number of negative ions produced by collisions in a period of time  $\tau$  is given by an integral of the form

$$A \int \left[ \iint n \, dx \cdot dy \right] \alpha \, dz,$$

where  $A$  involves  $w_1$  and  $\tau$ .

Hence the ratio,  $\mu$ , of the number of ions produced by collision inside the limits  $x = .2$  cm. and  $x = -.2$  cm. to the total number produced is

$$\frac{\int_0^{.2} dx \int_0^{.2} dz \int_{-\infty}^{\infty} n \, dy}{\int_0^{\infty} dx \int_0^{.2} dz \int_{-\infty}^{\infty} n \, dy} = \mu.$$

Since the emission of ions is confined to the central portion of electrode 2, it becomes apparent that for the larger values of  $\frac{Z}{k}$  the ions do not extend to the boundary (which is represented by  $\infty$ ). Hence at the boundary  $n=0$  and  $\frac{\partial n}{\partial y}=0$ . Equation (2) on integration with regard to  $y$  becomes

$$\frac{\partial^2 q}{\partial x^2} + \underbrace{\left[ \frac{\partial n}{\partial y} \right]}_{\text{boundary limits}} + \frac{\partial^2 q}{\partial z^2} - \gamma \frac{\partial q}{\partial z} + \gamma \cdot \alpha \cdot q = 0,$$

where  $q = \int n \, dy$ , the limits of integration being the values of  $y$  at opposite points on the boundary. Hence  $\left[ \frac{\partial n}{\partial y} \right] = 0$ .

Also since the ions for the larger values of  $\frac{Z}{k}$  move in a

narrow stream chiefly in the direction of the axis of  $z$ ,  $\frac{\partial^2 q}{\partial z^2}$  is small compared with  $\frac{\partial^2 q}{\partial x^2}$  or  $\gamma \frac{\partial q}{\partial z}$ .

Hence neglecting  $\frac{\partial^2 q}{\partial z^2}$  the above equation becomes

$$\frac{\partial^2 q}{\partial x^2} - \gamma \frac{\partial q}{\partial z} + \gamma \cdot \alpha \cdot q = 0,$$

or

$$\frac{\partial^2 \phi}{\partial x^2} = \gamma \frac{\partial \phi}{\partial z},$$

where

$$q = \phi e^{\alpha z}.$$

The solution is required to satisfy the following boundary conditions:

$$\left. \begin{aligned} \phi &= \text{constant from } x = \cdot 2 \text{ to } x = -\cdot 2 \text{ cm.} \\ \phi &= 0 \quad \text{when } x > \cdot 2 \quad \text{or} \quad < -\cdot 2 \text{ cm.} \end{aligned} \right\} z = 0.$$

Hence it is clear that  $\phi$  is a quantity which varies with  $x$  and  $z$  in the same way as the temperature  $\theta$  varies with  $x$  and the time  $t$ , in an infinite heat-conducting solid, whose initial condition is that, when  $t=0$   $\theta$  is zero everywhere except in an infinite slab bounded by planes  $x=\cdot 2$  cm. and  $x=-\cdot 2$  cm., where the temperature has a uniform value.

Therefore

$$\phi = A \int_{-\cdot 2}^{\cdot 2} z^{-\frac{1}{2}} e^{-\frac{\gamma(x-\xi)^2}{4z}} d\xi,$$

and

$$q = A e^{\alpha z} \int_{-\cdot 2}^{\cdot 2} z^{-\frac{1}{2}} e^{-\frac{\gamma(x-\xi)^2}{4z}} d\xi.$$

Hence  $\mu$  may be found by substituting this value of  $q$  in the equation

$$\mu = \frac{\int_0^{\cdot 2} dx \int_0^{\cdot 2} q dz}{\int_0^{\infty} dx \int_0^{\cdot 2} q dz} \dots \dots \dots (3)$$

This ratio is independent of  $\alpha$  when  $\alpha$  is small. The ratio  $\mu$  depends on  $\frac{Z}{k}$  since  $\gamma = \frac{Ne}{\Pi k} Z = 41 \cdot \frac{Z}{k}$ , where  $Z$  is expressed in volts per cm. The values of  $k$  corresponding to

different forces and pressures have been determined. Hence the values of  $\mu$  may be represented by a curve in terms of  $\frac{Z}{k}$ , when  $\alpha$  is small. The curve is shown in fig. 4.

The connexion between  $\mu$  and the quantity  $\rho$ , which is determined experimentally, may easily be found. Let  $n_0$  be the number of ions set free by the photo-electric effect,  $n_1$ ,  $n_2$ , and  $n_3$  the numbers of negative ions generated by collisions in the spaces  $S_1$ ,  $S_2$ , and  $S_3$  respectively.

Then

$$\mu = \frac{n_2}{n_1 + n_2 + n_3} = \frac{q_2}{q_1 + q_2 + q_3},$$

$$\rho = \frac{q_1 + q_3}{q_0 + q_2},$$

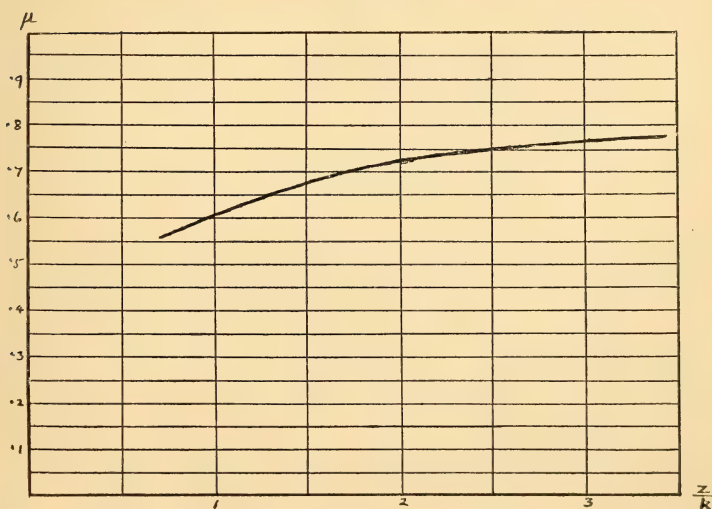
also

$$n_1 + n_2 + n_3 + n_0 = n_0 e^{2\alpha}.$$

Hence

$$e^{2\alpha} = \frac{(\rho + 1)(\mu - 1)}{\mu(\rho + 1) - 1}. \quad \dots \dots \dots (4)$$

Fig. 5.



Taking the case in which  $e^{2\alpha} = 1$  approximately, so that  $\mu$  is independent of  $\alpha$ , and is given by the curve in fig. 5 in



terms of  $\frac{Z}{k}$ , values of  $\alpha$  may be deduced by substituting these values of  $\mu$  in equation (4). It is interesting to notice that making  $e^{2\alpha}=1$  in evaluating the ratio  $\mu$  involves the assumption that the numbers of negative ions produced by collisions in spaces  $S_1$ ,  $S_2$ , and  $S_3$  are proportional to the numbers of the original ions, liberated from electrode 2, present in these spaces at any moment of time after the steady state has been reached. Let  $N_1$ ,  $N_2$ , and  $N_3$  be these numbers.

Then

$$u = \frac{n_2}{n_1 + n_2 + n_3} = \frac{N_2}{N_1 + N_2 + N_3} \dots \dots \dots (5)$$

The values of  $\mu$  corresponding to a given value of  $\frac{Z}{k}$  may be found as follows:

By giving  $\xi$  the values  $\cdot 2$ ,  $\cdot 1$ ,  $0$ ,  $\cdot 1$ , and  $\cdot 2$  successively the integrals are found to involve only

$$\int_0^a dx \int_0^2 z^{-\frac{1}{2}} e^{-10 \cdot 25 \frac{Z}{k} \cdot \frac{x^2}{z}} dz,$$

and

$$\int_0^\infty dx \int_0^2 z^{-\frac{1}{2}} e^{-10 \cdot 25 \frac{Z}{k} \cdot \frac{x^2}{z}} dz,$$

where  $a$  has the values  $\cdot 4$ ,  $\cdot 3$ ,  $\cdot 2$ , and  $\cdot 1$ .

If now  $z$  is given definite values, *e. g.*  $\cdot 1$ ,  $\cdot 5$ ,  $1$ ,  $1 \cdot 5$ , and  $2$ , the integrals involved are

$$\int_0^b e^{-\eta^2} d\eta \quad \text{and} \quad \int_0^\infty e^{-\eta^2} d\eta,$$

where  $b$  has certain numerical values.

These integrals can therefore be evaluated by the use of tables. The values of the original integrals after the  $\xi$  and  $z$  substitutions were plotted against  $z$ , and the values of the integrals, found by a calculation of areas, were plotted against the corresponding values of  $\xi$ . The ratio of the new areas gave the value of  $\mu$ .

When the values of  $\mu$  found from the curve in fig. 5, and the values of  $\rho$  taken from the curves in fig. 4, were substituted in equation (4), the following results were obtained.

TABLE I.

	$p=2$ mm.		$p=3$ mm.		$p=4$ mm.		$p=5$ mm.	
$\frac{Z}{p}$	$\frac{Z}{k}$	$\frac{\alpha}{p}$	$\frac{Z}{k}$	$\frac{\alpha}{p}$	$\frac{Z}{k}$	$\frac{\alpha}{p}$	$\frac{Z}{k}$	$\frac{\alpha}{p}$
40	...	...	...	...	1.77	.021		
45	...	...	1.42	.041	1.89	.044	2.36	.047
50	.98	.065	1.47	.069	1.96	.07	2.45	.076
55	1.01	.101	1.515	.105	2.02	.105	2.525	.11
60	1.04	.142	1.56	.145	2.08	.149	2.6	.17
70	1.09	.25	1.64	.28	2.188	.39		

It is observed that for a given value of  $\frac{Z}{p}$  the values of  $\frac{\alpha}{p}$  increase with the pressure, especially for the larger values of  $\alpha$ . This is not unexpected, since the relation expressed in (5) must cease to hold when  $\alpha$  is large. It is interesting to see how large  $\alpha$  may become before this relation ceases to be true (theoretically it is true as long as  $\frac{(2\alpha)^2}{2} + \frac{(2\alpha)^3}{3} + \dots$  may be neglected in comparison with  $1 + 2\alpha$  in the expansion of  $e^{2\alpha}$ ). Now if  $\alpha$  is known and substituted in (3) the value of  $\mu \left( = \frac{n_2}{n_1 + n_2 + n_3} \right)$  can be evaluated by a method similar to that explained above. In the case of the pressure of 2 mm. the values of  $\frac{\alpha}{p}$  were taken from Table I. for three values of  $\frac{Z}{p}$ .  $\alpha$  for each case was substituted in (3) as a first approximation. Values of  $\frac{n_2}{n_1 + n_2 + n_3}$  were thus obtained and were compared with the values of  $\frac{N_2}{N_1 + N_2 + N_3}$  for the corresponding values of  $\frac{Z}{k}$ .

TABLE II.

$\frac{Z}{p}$	$\frac{Z}{k}$	$\frac{N_2}{N_1 + N_2 + N_3}$	$\frac{n_2}{n_1 + n_2 + n_3}$	$\frac{\alpha}{p}$ (1)	$\frac{\alpha}{p}$ (2)
50	.98	.605	.602	.065	.065
60	1.04	.615	.598	.14	.134
70	1.09	.62	.593	.25	.226

Hence it appears that if  $\alpha$  does not exceed the value  $\cdot 13$  the relation (5) is very approximately true. The larger values of  $\alpha$  given in Table I. are too large, but if these values of  $\alpha$  are taken as first approximations to evaluate  $\frac{n_2}{n_1 + n_2 + n_3}$  ( $\mu$ ), and these values substituted in (4), more accurate values of  $\alpha$  can be found. The values of  $\frac{\alpha}{p}$  thus obtained are given in the last column of Table II., and for the sake of comparison the corresponding values of  $\frac{\alpha}{p}$  in Table I. are rewritten in the fifth column.

The following table gives a comparison of the values of  $\frac{\alpha}{p}$  obtained by this method with those found by F. W. Wheatley\*, who made use of a more direct method.

TABLE III.

$\frac{Z}{p}$	40	50	60	70
$\frac{\alpha}{p} \left\{ \begin{array}{l} \text{Wheatley} \dots \\ \text{Smith} \dots\dots\dots \end{array} \right.$	$\cdot 019$	$\cdot 055$	$\cdot 118$	$\cdot 212$
	$\cdot 021$	$\cdot 065$	$\cdot 134$	$\cdot 226$

If the values of  $\alpha$ , for larger values of  $\frac{Z}{p}$ , found by Prof. Townsend† are used to evaluate  $\mu$  from (3), and  $\mu$  is also found by substituting values of  $\alpha$  and  $\rho$  in (4), another interesting comparison may be made.

TABLE IV.

$\frac{Z}{p}$	$\frac{Z}{k}$	$\mu$ from (3)	$\mu$ from (4)
$p=2 \text{ mm.} \left\{ \begin{array}{l} 100 \\ 120 \end{array} \right.$	$1\cdot 25$	$\cdot 573$	$\cdot 576$
	$1\cdot 33$	$\cdot 556$	$\cdot 528$
$p=3 \text{ mm.} \quad 100$	$1\cdot 87$	$\cdot 606$	$\cdot 591$

\* Phil. Mag. Dec. 1913.

† Phil. Mag. June 1902.

In the case of  $\frac{Z}{p} = 120$ , and to a smaller degree in  $\frac{Z}{p} = 100$  for  $p = 3$  mm., the positive ions are probably producing ions by collisions to an appreciable extent. This would account for the value of  $\mu$ , obtained from (4), being smaller than the value found from (3), for expression (4) may be written

$$\mu = 1 - \frac{e^{2a}}{e^{2a} - 1} \cdot \frac{\rho}{1 + \rho},$$

so that

$$\delta\mu = -\lambda^2 \delta\rho,$$

and  $\delta\rho$  is positive if the positive ions generate ions by collisions.

When the apparatus was tested for small potential differences between the electrodes it was found that in some cases the electrodes 1 and 3 received negative ions. These ions must have diffused to 1 and 3 before they had time to acquire sufficient velocity in the direction of the electric force. The following table shows some of the results obtained for various pressures.  $V$  represents the potential difference between the electrodes in volts,  $\delta$  the deflexion of the electrometer when connected to the electrodes 1 and 3, and  $l$  the length in cm. of the mean free path of an electron in the gas. The ultra-violet light remained on for one minute in each case, and the deflexion was about 300 when the electrodes 1, 2, and 3 were all connected to the electrometer.

TABLE V.

$p = 2$ mm. $l = 0.16$ cm.			$p = .34$ mm. $l = .1$			$p = .044$ mm. $l = .8$			$p = .017$ mm. $l = 2$		
$V$	$\frac{Z}{p}$	$\delta$	$V$	$\frac{Z}{p}$	$\delta$	$V$	$\frac{Z}{p}$	$\delta$	$V$	$\frac{Z}{p}$	$\delta$
40	10	-4	13	20	-7	10.5	120	-8	10.5	309	-1
80	20	1	21	32	-3	17	193	-1.5	17	500	0
120	30	2.5	26.5	40	-1.5	21	238	1.5	19.5	573	.75
160	40	9.5	30.5	45.5	0	25	283	8	21	617	2
			34.5	52	2	...	...	...	25	735	7
			40	60	6						

It appears that as the pressure decreases a larger value of  $\frac{Z}{p}$  is necessary to prevent the negative ions from diffusing to the electrodes 1 and 3. This result is in accordance with



theory, for a decrease in the pressure of the gas causes an increase in the coefficient of diffusion of the ions into the gas. It seems reasonable to deduce from the above results that, with  $\frac{Z}{p}$  not less than 40, and for pressures of 2, 3, 4, and 5 mm., no appreciable number of negative ions can diffuse to the electrodes 1 and 3.

In conclusion it may be said that no great accuracy is claimed for the values of  $\frac{\alpha}{p}$  found in this investigation, but the experiments show directly the production of positive ions by collisions for small values of  $\frac{Z}{p}$  and for small potential differences between the electrodes, and also give some idea of the distribution of the current in a gas between parallel plate electrodes.

I desire to express my best thanks to Prof. Townsend, at whose suggestion the investigation was undertaken, for valuable advice given during its progress.

CIV. *The Theory of Molecular Volumes.*  
By GERVAISE LE BAS, B.Sc.\*

PART III.

THEORY OF PARTIAL RINGS.

*The Effect of Unsaturation. Residual Affinity.*

(A)  $\alpha$ ,  $\beta$ , and  $\gamma$  straight Chain Compounds.

STÄDEL (*Ber.* xv. p. 2259, 1889) showed that the  $\beta$  Halogen compounds always possess smaller volumes than the  $\alpha$ , and thus we have examples of molecules supposed to be structurally similar possessing different volumes.

The cause of this constitutive peculiarity, for it is undoubtedly such, was not further investigated.

It is a remarkable fact that the  $\alpha$  polysubstituted compounds all possess volumes which are comparable to those of monosubstituted compounds in that they follow the additive rule. They are thus normal.

\* Communicated by Prof. W. J. Pope, F.R.S.

*α Compounds.*

Compounds.	W.	M.V.	ΣA.V.	
$C_3H_7Cl$ .....	25	91.7	92.1	Cl 22.1.
$CHCl_3$ .....	23	84.5	84.8	
$CCl_4$ .....	28	103.7	103.2	
$CHBr_3$ .....	...	103.5	103.4	Br 28.3.
$CH_3 \cdot CHCl_2$ .....	24	88.9	88.6	
$CH_3 \cdot CCl_3$ .....	29	108.0	107.0	
$CCl_3 \cdot CHO$ .....	29	106.4	107.0	O 7.4 aldehydic.
$CClO \cdot CH_3$ .....	20	74.05	73.9	O 11.0 carboxylic.

Considering Stadel's regularity we find:

Ethidene Dichloride.

$\alpha$  (1, 1)  $CH_3 \cdot CHCl_2$ .

2  $CH_2$  ... 44.2

$Cl_2$  ... 44.2

ΣA.V ... 88.4

V ... 88.9

Ethylene Dichloride.

$\beta$  (1, 2)  $CH_2Cl \cdot CH_2Cl$ .

ΣA.V ... 88.4

V ... 85.3

Δ ... -3.1

84°0

B.P. ... 58°0

Propidene Dibromide.

$\alpha$  (1, 1)  $CH_3 \cdot CH_2 \cdot CHBr_2$ .

3  $CH_2$  ... 66.3

2 Br ... 56.6

ΣA.V ... 122.9

V ... 123.0

B.P. ... 133°0

Propidene Glycol.

$\alpha$  (1, 1)  $CH_3 \cdot CH_2 \cdot CH(OH)_2$ .

(unknown).

3  $CH_2$  ... 66.3

2 OH ... 22.2

ΣA.V. ... 88.5

B.P. ... —

Propylene Dibromide.

$\beta$  (1, 2)  $CH_3 \cdot CHBr \cdot CH_2Br$ .

ΣA.V ... 122.9

V ... 119.2

Δ ... -3.7

141°0.7

Propylene Glycol.

$\beta$  (1, 2)  $CH_3 \cdot CH(OH) \cdot CH_2(OH)$ .

ΣA.V. ... 88.5

V ... 85.37

Δ ... -3.13

188°5

Trimeth. Dibromide.

$\gamma$  (1, 3)  $CH_2Br \cdot CH_2 \cdot CH_2Br$ .

ΣA.V ... 122.9

V ... 118.1

Δ ... -4.8

165°0

Trimeth. Glycol.

$\gamma$  (1, 3)  $CH_2(OH) \cdot CH_2 \cdot CH_2(OH)$ .

ΣA.V. ... 88.5

V ... 84.2

Δ ... -4.3

214°0

Mr. Gervaise Le Bas on the  
Ethidene Diethyl Ether.

$$\begin{array}{rcl}
 & \text{CH}_3 \cdot \text{CH} (\text{OC}_2\text{H}_5)_2. & \\
 \text{C}_2\text{H}_5 \cdot \text{O} \mid & \text{C}_2\text{H}_5 & \dots\dots 106\cdot1 \\
 \text{C}_2\text{H}_5 \cdot \text{O} \mid & \text{C}_2\text{H}_5 & \dots\dots 106\cdot1 \\
 & \text{less } \text{C}_4\text{H}_{10} & \dots\dots -96\cdot0 \\
 & & \hline
 & & 116\cdot2 \\
 \text{plus } 2 \text{ CH}_2 & \dots\dots & 44\cdot2 \\
 & & \hline
 \Sigma \text{A.V.} & \dots\dots & 160\cdot4 \\
 \text{V.} & \dots\dots & 160\cdot2
 \end{array}$$

The following compounds are noteworthy :—

	M.V.	$\Sigma$ A.V.	$\Delta$ .
1, 2 CH <sub>2</sub> Br . CH <sub>2</sub> Br .....	97·6	100·8	-3·2
1, 2 CH <sub>2</sub> I . CH <sub>2</sub> Cl .....	101·3	103·3	-2·0
1, 2 CCl <sub>3</sub> . CO''Cl .....	125·5	129·1	-3·6
CH <sub>3</sub> . CO''Cl .....	74·0	73·9	—
1, 1 CH <sub>3</sub> . CH <sub>2</sub> . CHCl <sub>2</sub> .....	111·0	111·0	—
1, 2 CH <sub>3</sub> . CHCl . CH <sub>2</sub> Cl .....	107·9	111·0	-3·1
1, 3 CH <sub>2</sub> Cl . CH <sub>2</sub> . CH <sub>2</sub> Cl .....	106·0	111·0	-5·0
1, 1, 1 CH <sub>3</sub> . CCl <sub>3</sub> .....	108·0	107·0	—
1, 1, 2 CH <sub>2</sub> Cl . CHCl <sub>2</sub> .....	103·7	107·0	-3·3
1, 1, 2, 2 CHCl <sub>2</sub> . CHCl <sub>2</sub> .....	119·4	125·4	-6·0
1, 1, 1, 2, 2 CHCl <sub>2</sub> . CCl <sub>3</sub> .....	138·2	143·8	-5·6

The results furnished by the above investigation are exceedingly clear and uniform.

(a) If a paraffin compound be substituted by a halogen or other unsaturated substituent more than once, the volume of the compound is *normal* or subject to the additive rule, provided that the substituents be attached to a *single* C atom.

(b) If they are *distributed among several carbon atoms*, there are always *contractions* of a constitutive nature.

It matters not how many of the H atoms of the terminal C are substituted, the contractions are dependent upon the number in the  $\beta$  position which are substituted.

*For one substitution in the  $\beta$  position the contraction is a little over 3·0 units.*

*For two substitutions in the  $\beta$  position the contraction is about 6·0 units, or nearly double the first.*

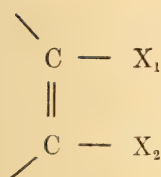
Substitutions in the  $\gamma$  (1, 3) position always involve greater contractions than substitutions in the  $\beta$  (1, 2) position; and it is conceivable that substitutions in the  $\delta$  (1, 4) position would result in still larger contractions.

Apparently it makes no difference what the substituent is so long as it is unsaturated. Thus, Cl, Br, I, OH, and probably  $\text{NH}_2$  and  $\text{COOH}$ , would all produce similar effects. Exception, doubly bound Oxygen, C : O.

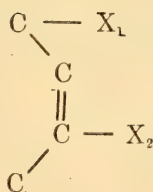
A possible and even probable feature of these constitutive effects is the difference in the attracting force between the different kinds of substituent. Consideration of this is only possible with more extended data. Moreover, the extent of the curvature is also a point for discussion. This would obviously be a consequence of the extent of the forces of attraction.

(B)  $\alpha\beta$ ,  $\alpha\gamma$ , and  $\alpha\delta$  substitutions in Ring Compounds.

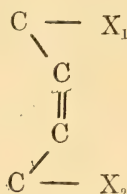
The *Isomers* of di-derivatives of Benzene are three in number :



1, 2 ortho -



1, 3 meta -



1, 4 para -

The compounds which illustrate the above and which have been sufficiently investigated for our purpose are fairly numerous, although it would be useful to possess data for the di-nitro, di-amino, di-chlor &c. compounds.

*Comparison of the Volumes of Benzene Derivatives.*

Compound.	Groups.	<i>o</i> (1, 1)	<i>m</i> (1, 2)	<i>p</i> (1, 3)	$\Delta$ .
Xylene, $\text{C}_8\text{H}_{10}$ .....	$\text{X}_1 = \text{CH}_3$ $\text{X}_2 = \text{CH}_3$	138.2	140.0	140.4	-2.2
Methyl Propyl B, $\text{C}_{10}\text{H}_{14}$ ...	$\text{X}_1 = \text{CH}_3$ $\text{X}_2 = \text{C}_3\text{H}_7$	—	184.9	184.9	—
Cresol, $\text{C}_7\text{H}_8\text{O}$ .....	$\text{X}_1 = \text{CH}_3$ $\text{X}_2 = -\text{OH}$	121.8	123.5	123.8	-2.0
Cresyl Meth. Oxide, $\text{C}_8\text{H}_{10}\text{O}$	$\text{X}_1 = \text{CH}_3$ $\text{X}_2 = -\text{OCH}_3$	146.4	147.7	148.0	-1.6
Cresyl Ethyl Oxide, $\text{C}_9\text{H}_{12}\text{O}$	$\text{X}_1 = \text{CH}_3$ $\text{X}_2 = -\text{OC}_2\text{H}_5$	171.2	172.4	172.4	-1.2
Cresyl Propyl Oxide, $\text{C}_{10}\text{H}_{14}\text{O}$	$\text{X}_1 = \text{CH}_3$ $\text{X}_2 = -\text{OC}_3\text{H}_7$	195.4	196.7	196.7	-1.3
Toluidene, $\text{C}_7\text{H}_9\text{N}$ .....	$\text{X}_1 = \text{CH}_3$ $\text{X}_2 = -\text{NH}_2$ ...	126.9	128.3	128.9	-2.0
Nitrotoluene, $\text{C}_7\text{H}_7\text{NO}_2$ .....	$\text{X}_1 = \text{CH}_3$ $\text{X}_2 = -\text{NO}_2$ ...	142.6	144.3	145.2	-2.6



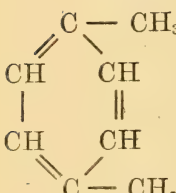
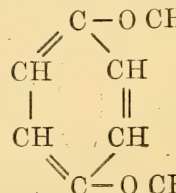
These results show :—

(a) That there is always a contraction when the substituents are in the ortho- or 1 : 2 position ; that is, when they are nearest to each other.

This is apparently a regularity similar to that involved in substitutions in the 1 : 2 position in open-chain compounds, although the influence of residual affinity must be less, owing to partial saturation of the substituents. In the above table the contractions are  $< 2.0$ . In the case of nitrotoluene the contraction is greater,  $-2.6$ , probably owing to the great influence of the  $\text{NO}_2$  group.

The explanation to follow is not affected by considerations connected with the spatial arrangement of the atoms and groups. The two groups in the above table are considered to be on the same side of the ring. It would be interesting to know how the two geometrical isomerides differ as regards volume.

(b) Meta 1 : 3 substitutions show small contractions, and para 1 : 4, which are normal, none at all.

<i>p</i> -Xylene.				Dimethyl Resorcin.			
	$\text{VC}_6\text{H}_4$	89.6			$\text{VC}_6\text{H}_4$	89.6	
	$2 \text{CH}_3$	51.2			$2 \text{CH}_3\text{O}$	66.6	
	$\Sigma \text{ A.V.}$	140.8			$\Sigma \text{ A.V.}$	156.2	
	V	140.4			V	157.1	

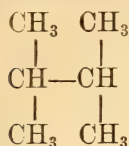
(c) *In Ring Compounds the contractions diminish as the substituents are removed the further away from each other.*

### (C) *Explanation of Constitutive Effects.*

Having pointed out two important constitutive effects in open-chain and closed-chain compounds, we attempt their explanation. The following differences to be observed in different cases will assist in the elucidation of the problem.

In open-chain compounds they increase. This is an important distinction, and since the result in the case of ring compounds is what we should expect, the peculiarity in the case of open-chain compounds calls for special explanation.

One or two cases occur in the latter which follow the same rule as for ring compounds, and this will help us at arriving at a solution of the difficulty.

Diisopropyl ( $C_6H_{14}$ ).V normal  $C_6H_{14}$  139.93

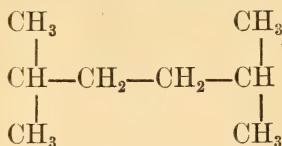
V diisopropyl 136.9

$$\Delta \dots -3.03$$

*n*-Heptane  $C_7H_{16}$  ... 162.92

Isoheptane ... 162.34

$$\Delta \text{ for Iso Group} \quad -0.58$$

Diisobutyl ( $C_6H_{14}$ ).V normal  $C_6H_{14}$  186.26

V diisobutyl 185.20

$$\Delta \dots -1.06 = 2 \times 0.53$$

In the case of diisobutyl, the difference in volume from the normal compound is about twice the contraction for the iso-group. In the case of diisopropyl, the contraction is considerably greater.

It is reasonable to suppose that in this case the iso-groups are so close that they interfere with each other, but that when two methylene groups intervene the possibility of interaction is diminished.

So also is this the case with ring compounds. In the ortho position the substituents are so close that they attract each other and so cause diminutions in volume. In the meta- and especially in the para-positions, the substituents cannot so readily interact, as they are further removed and for the most part outside of the range of each other's attractions.

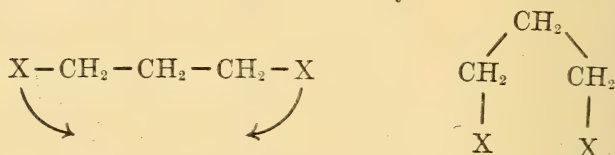
In both of the above cases by no possibility can the general configuration of the molecule be altered, for in ring compounds, which already possess a definite and stable configuration, this is seen to be impossible, and in the diiso-paraffins the substituents ( $\text{CH}_3$  groups) are symmetrically disposed and balance each other.

We are left to account for the anomalous behaviour of  $\beta$  and  $\gamma$  di-substitution derivatives of the paraffins which show *increased* contractions, the further they are removed from each other.

This peculiarity can readily be explained by means of this theory of *Residual Affinity* which we are considering, and which has been so fruitful in the hands of Thiele under the name of *Partial Valency*.

We must suppose that the attractive force between the

two substituents acts in the direction of causing curvature of the C chains where this is necessary.



That attractive forces of sufficiently powerful nature are possible, is seen from the fact that all the unsaturated groups possess latent valencies, *e. g.*, Cl, Br, I, OH, as also  $\text{NO}_2$ ,  $\text{NH}_2$ ,  $\text{COOH}$ .

It is apparently necessary for the unsaturated groups to be singly linked to the carbon atoms, so as to possess sufficient mobility. Doubly linked atoms lack this mobility and thus do not contribute to the constitutive effect. We find an example in : O.

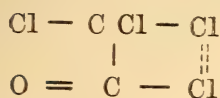
Groups like  $\text{CH}_3-$ ,  $\text{C}_2\text{H}_5-$ ,  $\text{CH}_3\text{O}-$ , are usually supposed to be saturated, but probably are not so. The attractive force might not be sufficiently powerful to change the configuration of hydrocarbon chains, but two such groups in proximity would doubtless attract each other.

This subject can only be adequately dealt with, when a more extended body of data is available.

The configurations of the compounds thus are :—

Ethylene dichloride.	Propylene Glycol.	Ethylene bromide.
$  \begin{array}{c}  \text{CH}_2 - \text{Cl} \\    \quad \quad \quad \parallel \\  \text{CH}_2 - \text{Cl}  \end{array}  $	$  \begin{array}{c}  \text{CH}_3 - \text{CH} - \text{OH} \\    \quad \quad \quad \parallel \\  \text{CH}_2 - \text{OH}  \end{array}  $	$  \begin{array}{c}  \text{CH}_2 - \text{Br} \\    \quad \quad \quad \parallel \\  \text{CH}_2 - \text{Br}  \end{array}  $
Contraction		
$\Delta \dots -3.1$	$-3.13$	$-3.2$
Trimethylene bromide.	Trimethylene Glycol.	Trimethylene chloride.
$  \begin{array}{c}  \text{CH}_2 - \text{Br} \\  \diagup \quad \quad \parallel \\  \text{CH}_2 \quad \quad \text{CH}_2 - \text{Br} \\  \diagdown \quad \quad \parallel  \end{array}  $	$  \begin{array}{c}  \text{CH}_2 - \text{OH} \\  \diagup \quad \quad \parallel \\  \text{CH}_2 \quad \quad \text{CH}_2 - \text{OH} \\  \diagdown \quad \quad \parallel  \end{array}  $	$  \begin{array}{c}  \text{CH}_2 - \text{Cl} \\  \diagup \quad \quad \parallel \\  \text{CH}_2 \quad \quad \text{CH}_2 - \text{Cl} \\  \diagdown \quad \quad \parallel  \end{array}  $
$\Delta \dots -4.8$	$-4.3$	$-5.0$
Chlorethylene dichloride.	Tetrachlorethane.	Pentachlorethane.
$  \begin{array}{c}  \text{Cl} - \text{CH} - \text{Cl} \\    \quad \quad \parallel \\  \text{CH}_2 - \text{Cl}  \end{array}  $	$  \begin{array}{c}  \text{Cl} - \text{CH} - \text{Cl} \\  \parallel \quad   \quad \parallel \\  \text{Cl} - \text{CH} - \text{Cl}  \end{array}  $	$  \begin{array}{c}  \text{Cl} - \text{C} - \text{Cl} - \text{Cl} \\  \parallel \quad   \quad \parallel \\  \text{Cl} - \text{CH} - \text{Cl}  \end{array}  $
$\Delta \dots -3.3$	$-6.0$	$-5.6$

Trichloroacetyl chloride.

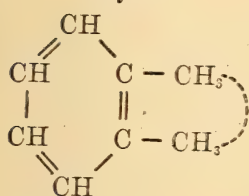


Contraction

$$\Delta \dots -3.6$$

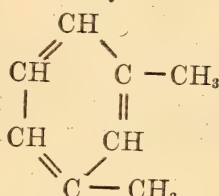
As regards the Ring Compounds, we find:—

*o*-Xylene.



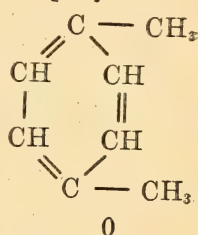
$$\Delta \dots -2.2$$

*m*-Xylene.



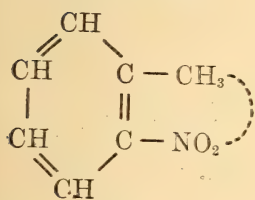
$$-0.4$$

*p*-Xylene.



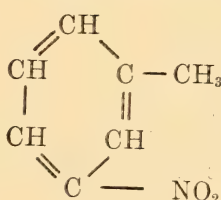
$$0$$

*o*-Nitrotoluene.



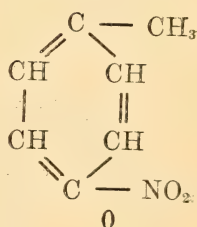
$$\Delta \dots -2.6$$

*m*-Nitrotoluene.



$$-0.9$$

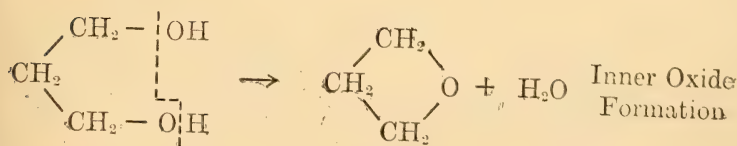
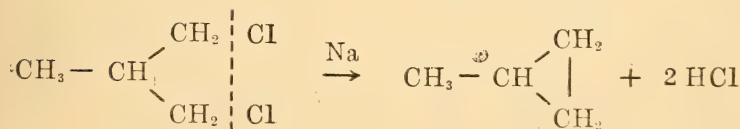
*p*-Nitrotoluene.



$$0$$

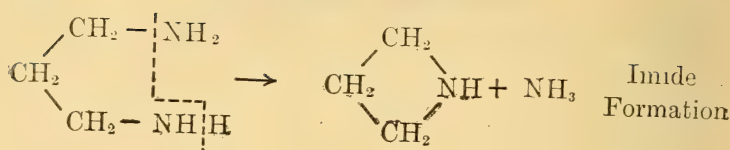
So far all the facts available favour our hypothesis, but certain other pieces of evidence make it stronger.

(a) It is well known that di-derivatives of the paraffins by means of suitable reagents form ring compounds.



Inner Oxide  
Formation

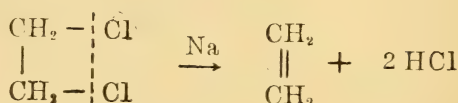




and so on in many other cases.

(b) It has been concluded (*Ber.* xv. p. 630, 1882) from the peculiar differences in the deportment of the  $\alpha$ ,  $\beta$ , and  $\gamma$  oxy acids, when they split off water to form lactones, that in these oxy acids there is a special spatial arrangement or configuration of the C chains. The assumption that the atoms of a molecule not linked to each other in a formula can exert an affinity upon one another, has led to the idea that in a union of more than two C atoms these atoms arrange themselves, not in a straight line, but upon a curve.

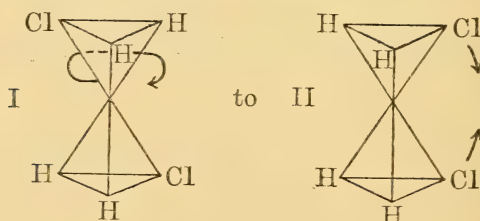
(c) In the ethylene compounds it is impossible for ring-compounds to form unless polymerization occurs, in some cases at least :—



The product is the unsaturated compound Ethylene. The presumption is strongly in favour of the contiguous position of the two Cl atoms in the original compound.

### Carbons Singly Linked.

The possibility of isomerism at first sight seems clear :—

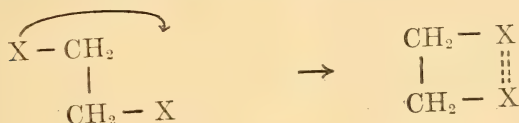


by Rotation.

If we suppose that rotation on the single axis joining the two carbons can take place easily, we see that Form I. would be unstable and tend to pass into Form II. by this

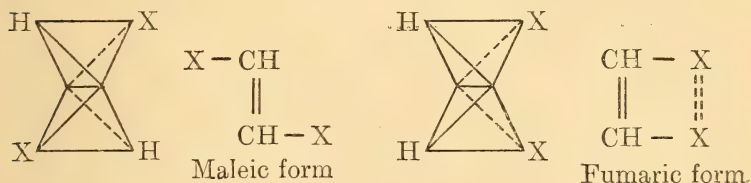
self-same process. In practice only one (Form II.) would be possible. As a matter of fact, only one ethylene di-substitution product is known.

On the plane we represent the change :—



### Carbons Doubly Linked.

When the carbons are doubly linked, rotation cannot occur for the reason that this would take place against a resistance offered by a field of force in the region between the two C atoms. Thus the two isomers are more or less stable and are indeed found. This is indicated by the well-known diagrams :—



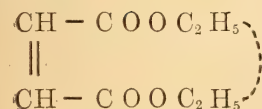
The two forms according to our hypothesis would possess different volumes and boiling-points. The fumaric modification would follow the Additive Rule, and the maleic modification would be subject to a contraction.

This is indeed the case if we are to judge by the densities at ordinary temperatures.

### Maleic Ester.

### Fumaric Ester.

#### Ethyl.



$d_{20}$  (Knops)... 1.06917  
 B.P. .... 225° C.  
 $V_{\text{B.P.}}$  (calc.) .. 194.9

$d_{20}$  (Knops)... 1.05199  
 218° C.  
 197.6

$\Delta$  ..... -2.7

<i>Propyl.</i>	Maleate.	Fumarate.
$d_{20}$ .....	1.02899	$d_{20}$ ..... 1.02203
	Ethyl Citraconate.	Ethyl Mesaconate.
	$\text{CH}_3-\text{C}-\text{COOC}_2\text{H}_5$	$\text{COOC}_2\text{H}_5-\text{C}-\text{CH}_3$
	$\parallel$	$\parallel$
	$\text{HC}-\text{COOC}_2\text{H}_5$	$\text{HC}-\text{COOC}_2\text{H}_5$
$d_{20}$ (Knops) ...	1.06241	$d_{20}$ ..... 1.04674

*Solution Volumes.*(Traube, *Ann.* 240. p. 43, 1886.)

## Sodium.

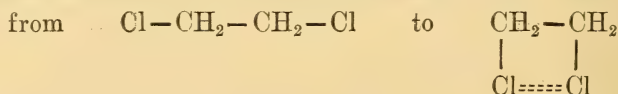
Maleate.		Fumarate.
$V_{15}$ ..... 54.3	$\Delta$ ..... -5.1	59.4
Citraconate.		Mesaconate.
$V_{15}$ ..... 66.5	$\Delta$ ..... -4.1	70.6
Crotoconate.		Isocrotoconate.
$V_{15}$ ..... 62.4	$\Delta$ ..... -2.0	64.4

All these results are in favour of our view. The malenoid compounds are marked by a contraction and a higher B.P. than the fumaroid, similar, indeed, to what is shown by the  $\alpha$  and  $\beta$  di-substitution compounds. These features are accompanied by the possibility of forming the ring compound in the malenoid form—Maleic anhydride, Citraconic anhydride.

The above data are for 20°. No data exist for the B.P. It must be remembered that the contractions are considered to be the result of Residual affinity, and since the groups  $-\text{C}.\text{OOR}$  are nearly saturated, the contractions may not be large in these instances.

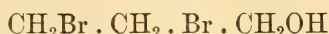
It thus seems clear that the constitutions which we give to the above geometrical Isomers, and which account for certain peculiarities, must be given to the  $\beta$ -derivatives of the Paraffins, since similar physical peculiarities are shown.

In carbon chains of greater length than two, curvature is an additional fact which must be taken into consideration. The tendency of the Cl atoms, say, to approximate even in ethylene derivatives, constitutes a curvature of the chain



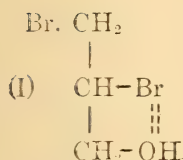
No doubt this regularity which we are discussing is capable of elucidating the constitution of unknown compounds.

$\alpha\beta$  Dibrom alcohol according to Weger (*Ann.* 221. p. 61) has a volume at the B.P. of 124.3.

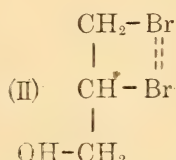


is the ordinary formula.

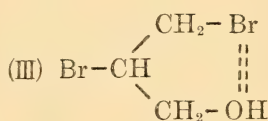
The possible formulæ are, on our hypothesis,



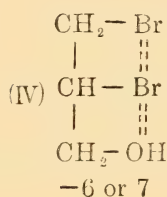
$\alpha$   
Contraction -3.1



$\beta$   
-3.1



$\gamma$   
-4.5



Volume of $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2\text{OH}$ .....	81.5
less 2H .....	7.4
	<hr/>
	74.1
plus 2Br .....	56.6
	<hr/>
$\Sigma \text{AV}$ .....	130.7
V .....	124.3
	<hr/>
$\Delta$ .....	-6.4
	<hr/>

The formula of Weger's Dibrom alcohol is thus Number IV. (probably) and is strictly analogous to the Tri-Hydroxy compound Glycerol. Tri-chlor and Tri-brom Hydrin would be similar.



The following compound is also interesting in this connexion:—

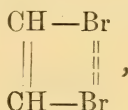
Acetylene Dibromide  $C_2H_2Br_2$ .

M.V. .... 91.3       $\Sigma$ M.V.<sub>a</sub> ..... 93.0    if   Br=28.0

$\Delta$  ... -1.7

$C_2H_4Br_2$  gives  $\Delta$  -3.1.

We must thus suppose that the formula is

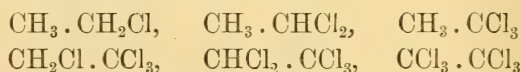


but that the olefin linking diminishes the value of  $\Delta$ .

### *The Effect of Chlorinating Benzene.*

One aspect of the work in this section is the successive chlorination of the Paraffins.

Take for instance *ethane*  $C_2H_6$ . By successive chlorination we obtain the compounds



The result is to show that only the  $\alpha$  compounds are normal; the  $\beta$  compounds are marked by a contraction in volume which is the result, it is contended, of the formation of Partial Rings—or, perhaps, from another point of view Temporary Rings.

The question now is, what may be the effect of successively chlorinating benzene  $C_6H_6$ ? We are able to answer this question, to some extent at any rate, owing to the work of Jungfleisch (*Jahresberichte*, xx. p. 36, xxi. p. 352).

### *Monochlorbenzene.* $C_6H_5Cl$ .



(Unsymmetrical or Odd).    M.V. 114.6.  
B.P. 132°0.

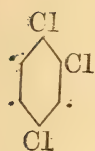
$$Cl = C_6H_5Cl - C_6H_6 = 114.6 - 92.8 = 21.8.$$

### 1 : 4 *Dichlorbenzene.* $C_6H_4Cl_2$ .

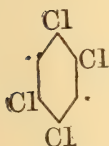


(Symmetrical or Even).    M.V. 130.9.  
B.P. 172°0.

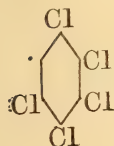
$$Cl_2 = C_6H_4Cl_2 - C_6H_6 = 130.9 - 89.6 = 41.3.$$

1:2:4 Trichlorobenzene.  $C_6H_3Cl_3$ .(Unsymmetrical or Odd). M.V. 149·1.  
B.P. 213°·0.

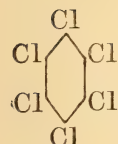
$$Cl_3 = C_6H_5Cl_3 - C_6H_3 = 149\cdot1 - 86\cdot4 = 62\cdot7.$$

1:2:4:5 Tetrachlorobenzene.  $C_6H_2Cl_4$ .(Symmetrical or Even). M.V. 165·0.  
B.P. 244° C.

$$Cl_4 = C_6H_2Cl_4 - C_6H_2 = 165\cdot0 - 83\cdot2 = 81\cdot8.$$

1:2:3:4:5 Pentachlorobenzene.  $C_6HCl_5$ .(Unsymmetrical or Odd). M.V. 183·8.  
B.P. 276°·0.

$$Cl_5 = C_6HCl_5 - C_6H = 183\cdot8 - 80\cdot0 = 103\cdot8.$$

Hexachlorobenzene.  $C_6H_6$ .(Symmetrical or Even). M.V. 200·0.  
B.P. 326°·0.


$$Cl_6 = 200\cdot0 - 76\cdot8 = 123\cdot2.$$

If we subtract the values of the Cl atoms we obtain the following results :—

Compound.	$n$ .	$V n Cl$ .	$\Delta$ .
$C_6H_5Cl$ .....	1	21·8	19·5
$C_6H_4Cl_2$ .....	2	41·3	21·4
$C_6H_3Cl_3$ .....	3	62·7	19·1
$C_6H_2Cl_4$ .....	4	81·8	22·0
$C_6HCl_5$ .....	5	103·8	19·4
$C_6Cl_6$ .....	6	123·2	

Thus we have :—

	Normal. (Unsymm. or Odd).	Abnormal. (Symm. or Even).
1st Chlorine atom Cl <sub>i</sub> .....	21·8	—
2nd Chlorine atom Cl <sup>ii</sup> .....	—	19·5
3rd Chlorine atom Cl <sup>iii</sup> .....	21·4	—
4th Chlorine atom Cl <sup>iv</sup> .....	—	19·1
5th Chlorine atom Cl <sup>iv</sup> .....	22·0	—
6th Chlorine atom Cl <sup>v</sup> .....	—	19·4
Mean .....	21·8	19·3

If we arrange the Normal and Abnormal Cl atoms on a diagram and enclose the latter by a circle thus  we find :—



The abnormal Cl atoms are situated in the para positions relative to each other, and the effect is to make one half of the molecule substituted by Cl atoms normal and the other half abnormal.

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CV. *Note on some Modifications in an ordinary Balance which conduce to ease and quickness of weighing.* By G. A. SHAKESPEAR, M.A., D.Sc.\*

**H**AVING had occasion during the last two years to use a balance for rapid and somewhat accurate weighings, I have been led to make certain modifications in the ordinary instrument. The result has been so satisfactory in practice that I think it may be worthwhile describing the arrangement.

In the use of a good physical balance the accuracy of weighing is mainly limited by (a) the accuracy of the weights, (b) constancy of temperature in the balance case, (c) the accuracy with which the position of the rider can be

\* Communicated by Sir Oliver Lodge, F.R.S.

read, and (d) the magnitude of the smallest measurable deflexion of the beam. Weighings are often made, even by skilled observers, in which details (a) and (b) are not sufficiently regarded, and a degree of accuracy which is quite illusory is apparently obtained. When a centigramme rider is used, it is generally possible to estimate the small changes of weight, due to changing the position of the rider, to a degree of accuracy far beyond that which is warranted in view of the uncertainty as to the conditions (a) and (b). Theoretically, the sensitiveness may be increased so that the smallest appreciable change of position of the rider produces an observable deflexion of the beam. In practice, however, it is found advisable to have a degree of sensitiveness for which a comparatively large change of position of the centigramme rider produces no appreciable change in deflexion. In other words, the rider is usually too small and the means of measuring deflexion not sufficiently delicate. In the balance to be described the rider is therefore comparatively large (either .5 gm. or .05 gm.), and the deflexion is observed optically by using a concave mirror attached to the beam.

The effect is to provide a pointer of considerable length but with small mass and moment of inertia, so that the period of oscillation is appreciably reduced. There is, moreover, no parallax.

*Rider Beam.*—This runs from end to end of the beam, the upper edge being in the plane of the knife-edges. It is divided into ten equal divisions each of which is subdivided into ten smaller divisions.

*Rider.*—This is in the form of an elongated ring which surrounds the rider beam (thus preventing possibility of falling off) and provided with a hook at its upper part. When the balance is unloaded and in equilibrium the rider is at zero mark on the left side of its beam. It may be either .5 gm. or .05 gm., giving respectively 1 cgm. or 1 mgm. for one small division; the smallest weights in the box are then 1 gm. or .1 gm. Tenths of a division can, of course, be estimated.

*Method of moving the Rider.*—The rider is moved by means of a thin silk cord (plaited fishing-line is good) passing through a slit at each end of the case. The shape of the slit is shown at A in the figure, the upper part being vertical and in the same plane as the rider beam but rising above the level of the top of the rider. The lower part of the slit slopes downwards and forwards. The silk cord has a small stretching-weight at each end, and when at rest these



weights pull the cord to the lower ends of the slits, thus keeping it taut and clear of the beam. To move the rider the cord is grasped by both hands, one at each end, and is raised. It thereupon automatically engages the hook of the rider and lifts the latter from its beam. By sliding the cord along, the rider can then be adjusted with ease and precision, and the cord falls clear again when released. To facilitate grasping with the fingers, the cord is made to pass over a small projecting bar outside each slit, as shown in the figure at B.

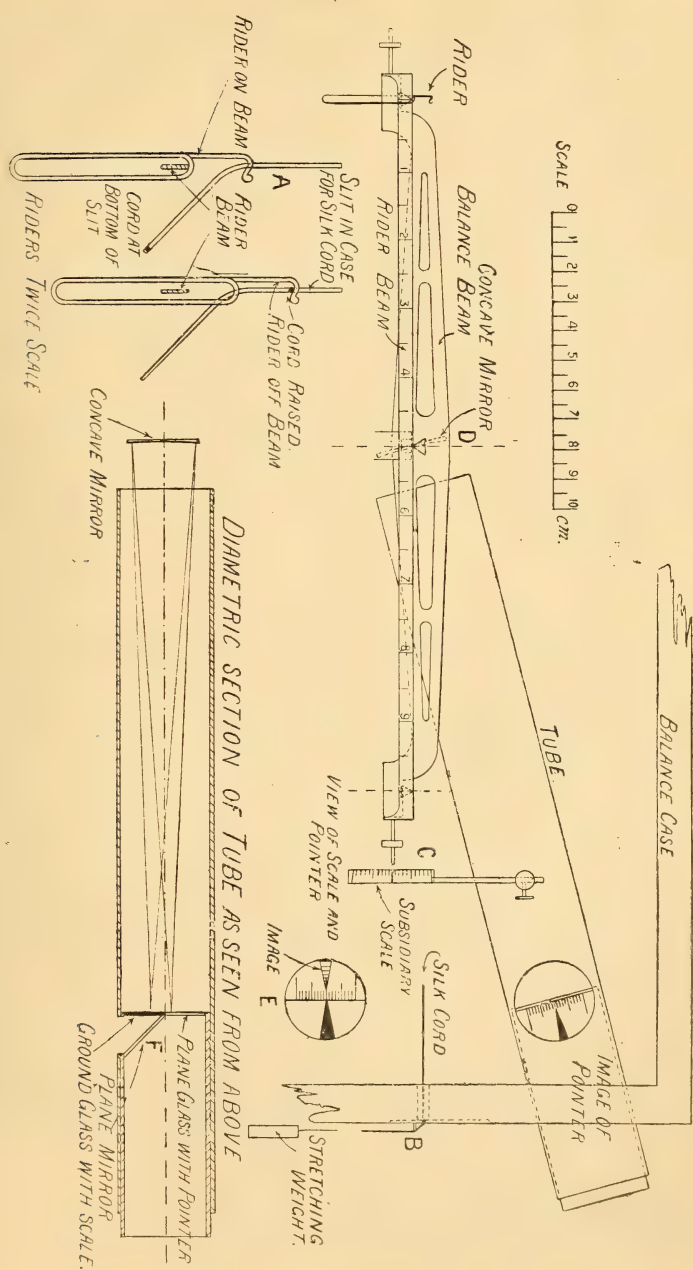
When the cord becomes worn, minute particles of silk may occasionally stick to the rider. This is unimportant unless the rider is very small, but the trouble can be obviated entirely by replacing a short length of the cord with a piece of thin wire which can always be brought into contact with the rider in place of the silk.

*Pointer.*—For rough adjustment, a projection at one end of the beam moves near a fixed scale (as shown at C). For fine adjustment, a thin concave mirror is fixed to the back of the beam, a diameter of the mirror being in line with the axis of rotation of the beam. The plane of the mirror may be vertical or inclined at an angle to the vertical. A slightly inclined position, shown in the diagram at D, is found convenient. A tube passes through the wall of the case and reaches nearly to the mirror, the axis of the tube nearly coinciding with that of the mirror. Sliding into this tube is a shorter length which carries a plane piece of glass at right angles to the axis of the tube. One half of this glass is slightly ground and has engraved on it a scale. On the other half is fixed a pointed piece of foil, the point coming opposite to the middle of the scale (as shown at E).

The small tube is slid into the larger one until the point of the foil and the centre of the scale are at conjugate foci of the mirror, and the image of the point is thus cast on to the scale. To enable the image of the scale to be seen from the front, an aperture is made in the front side of the tube and a piece of plane mirror is put at an angle of  $45^\circ$  behind the scale (as shown in plan at F).

To illuminate the mirror the balance may be placed with the tube directed towards a window; but a plane mirror capable of turning about an axis at right angles to that of the tube and fitted to the latter by means of a collar which can be turned about the outer end of the tube, enables light from any source to be used (this is not shown in the figure).

The arrestment of the balance should be of the type (found in most good balances) which only raises the beam a fraction of a millimetre.



In weighing, the weights are placed in the right-hand pan, the rider being at its zero mark. Weights to the nearest gramme (less than the weight of body) are put into the pan if the half-gramme rider is used; the case is closed, and the fractions of a gramme are given by one setting of the rider.

The sensitiveness of the balance should be so adjusted that the smallest readable change of position of the rider gives the smallest readable change of deflexion.

Experiment shows that even in a very draughty room currents of air through the slits do not introduce errors unless very delicate measurements are being made. Such currents can be prevented by having a second slit in another piece of metal pivoted so that the cord can pass through the intersection of the two slits.

The diagram represents a cheap form of balance which has been fitted in the workshop with the modifications described.

No new principle is involved, but a balance so fitted has been found to give great saving of time and labour in weighing.

CVI. *On a Theory of the Rotational Optical Activity in Isotropic Media.* By G. H. LIVENS\*.

**I**N some recently published papers† the author, starting from a suggestion originally made by H. A. Lorentz, has given indications towards a new form of the electron theory of the optical rotatory power in isotropic media. The results obtained are in such close agreement with the experimental facts that there can hardly be any doubt as to the correctness of the fundamental assumptions on which they are based. The object of the present paper is to give now as complete a statement of the theory as possible, in the hope that it may lead to further experimental investigations of its appropriateness.

In the modern electromagnetic theory of optics we have always to deal with the electric and magnetic force and the electric and magnetic flux, such that each flux is derived from the other force by the universally valid circuital relations. If we denote the electric and magnetic force vectors by  $E$  and  $H$  respectively and the corresponding fluxes by  $D$  and

\* Communicated by the Author.

† "On Rotational Optical Activity of Solutions," *Phil. Mag.* June 1913.

B, these relations are expressed by the following vector equations

$$-\frac{1}{c} \dot{\mathbf{B}} = \text{Curl } \mathbf{E}, \quad \frac{1}{c} \dot{\mathbf{D}} = \text{Curl } \mathbf{H}, \quad \dots \quad (1)$$

wherein the Hertz-Heaviside units are adopted and  $c = 3 \cdot 10^{10}$  is the velocity of light *in vacuo*.

The influence of the molecules of the medium expresses itself only on the form of the relations, depending on the constitution of the medium, connecting each flux with the corresponding force. Since in light phenomena we can always take  $\mathbf{B} = \mathbf{H}$ , we need only to investigate the relation between  $\mathbf{D}$  and  $\mathbf{E}$ . This is obtained, as in Drude's theory, by a statistical analysis of the motions of the contained electrons, to which the electric flux due to the presence of the medium is directly reducible. These electrons are, as usual, supposed to be connected to the molecules of the medium by quasi-elastic forces, and are resisted in their motion by frictional forces proportional to their velocity. The equations of motion of such electrons are therefore of a type

$$m(\ddot{s}_r + n_r' \dot{s}_r + n_r^2 s_r) = e \mathbf{F}_s,$$

wherein  $s_r$  is the vectorial displacement of the electron from its position of equilibrium;  $m$  is its mass and  $e$  the charge on it;  $mn_r^2$  is the parameter of the quasi-elastic force and  $mn_r'$  that of the frictional resistance. The force  $\mathbf{F}_s$  is the component force (parallel to direction of displacement) on the contained electron due to the electric field in the incident light wave.

In the usual, Drude's, form of the theory one simply takes  $\mathbf{F} = \mathbf{E}$ ; but Lorentz has shown\* that the force on the contained electron is not thereby completely represented; we must in fact add a term  $f(\mathbf{P})$ , where  $f(\mathbf{P})$  denotes some undetermined vector function of the polarization intensity  $\mathbf{P}$  in the medium. As a first approximation for isotropic media it is shown that  $f(\mathbf{P}) = a\mathbf{P}$ , where  $a$  is very nearly equal to  $1/3$ ; but in second order effects of the kind under discussion other terms may occur. In order to explain the broad general facts of the phenomena at present under review it is in fact necessary to assume, with Lorentz, that

$$f(\mathbf{P}) = a\mathbf{P} + b \text{Curl } \mathbf{P},$$

the constant  $b$  being some physical constant of the medium

\* 'Versuch einer Theorie der elekt. u. opt. Erscheinungen, &c.' (Leipzig, 1906) pp. 78-81.



determining the extent of the effect of its asymmetric structure on its optical behaviour.

This simple statement, however, seems to require a little more precision. Does the constant  $b$  depend on the relative density of the chirally active molecules? Or does this second order force not act equally on all the electrons in the medium? It seems difficult to realize that this force, originating in the chiral structure of the active molecules, can be appreciable equally well at any point of a medium throughout which the actual chiral molecules are but sparsely distributed. This leads to the view I have formerly adopted, that this chiral part of the force is appreciable only in the immediate neighbourhood of the optically active molecules. There is of course the alternative and practically equivalent view that the presence of so many active molecules imparts a slight chiral structure to the whole medium, and to an extent depending on the relative density of such molecules\*. In the actual analysis I shall adopt my former view, and for simplicity will assume this force to be perceptible only for those electrons contained within the active molecules.

We have thus in isotropic media

$$\mathbf{F} = \mathbf{E} + a\mathbf{P} + b \text{Curl } \mathbf{P},$$

and with this form the equations of motion of the typical electron are of the form

$$m(\ddot{s}_r + n_r' \dot{s}_r + n_r s_r) = e(\mathbf{E}_s + a\mathbf{P}_s) + b \text{Curl}_s \mathbf{P}.$$

If now the light incident on the body is a simple harmonic wave-train of frequency  $n$ , the electrons are compelled by the electric force in the incident beam, with more or less

success, to vibrate with a period  $\frac{2\pi}{n}$ . Thus the functions

may all be considered to depend on the time by the exponential factor  $e^{int}$ , so that we have

$$m(-n^2 + in n_r' + n_r^2) s_r = e(\mathbf{E}_s + a\mathbf{P}_s) + b \text{curl}_s \mathbf{P}.$$

By solving this equation for  $s_r$  we determine the position of the typical electron corresponding to the values  $\mathbf{E}$  of the electric force and  $\mathbf{P}$  of the polarization. By forming the vectorial sum  $\sum e s_r$  per unit volume, which we know is equal to  $\mathbf{P}_s$ , we obtain a relation between the electric force and

\* On due consideration I think this alternative view untenable as there would then be no distinction between chirally active electrons and non-chirally active ones; a distinction which is required by the results of some of Cotton's experiments.

polarization intensity, the coefficients being in general complex functions of the light disturbance considered. This relation is of the form

$$P = \left( \sum \frac{e^2/m}{n_r^2 + inn_r' - n^2} \right) (E + \alpha P) + \left( \sum' \frac{be^2/m}{n_r^2 + inn_r' - n^2} \right) \text{Curl } P,$$

wherein  $\Sigma'$  denotes a sum taken only over the electrons contained in the actual active molecules and perhaps only over some of them.

Lorentz writes this relation in the form

$$E = \alpha P + \beta \text{curl } P,$$

without giving any account of the constants  $\alpha, \beta$ ; our theory shows that

$$\alpha = \frac{1 - \sum \frac{ae^2/m}{n_r^2 + inn_r' - n^2}}{\sum \frac{e^2/m}{n_r^2 + inn_r' - n^2}}, \quad \beta = - \frac{\sum' \frac{be^2/m}{n_r^2 + inn_r' - n^2}}{\sum \frac{e^2/m}{n_r^2 + inn_r' - n^2}}.$$

We can now obtain the required constitutional relation to complete the scheme of equations for our medium. We know in fact that

$$D = P + E,$$

and thus

$$E(1 + \alpha) - \beta \text{Curl } E = \alpha D - \beta \text{Curl } D \quad . \quad . \quad (2)$$

is the required relation.

Now let us examine the propagation of a plane homogeneous beam of light in a medium where these relations are satisfied. The direction of propagation is taken to be the axis of  $z$  in a rectangular coordinate system so that the components of  $E, D, H$  all involve the coordinates of space

and time only by the exponential factor  $e^{in(t - \frac{z}{c})}$ , wherein  $q$  is in general a complex constant, a function of  $n$ , the frequency of the light used.

Since all differentials with respect to  $(x, y)$  vanish, the general equations (1) reduce to

$$-\frac{1}{c} \frac{dH_x}{dt} = \frac{\partial E_y}{\partial z}, \quad -\frac{1}{c} \frac{dH_y}{dt} = -\frac{\partial E_x}{\partial z}, \quad H_z = 0,$$

and

$$\frac{1}{c} \frac{dD_x}{dt} = \frac{\partial H}{\partial z}, \quad \frac{1}{c} \frac{dD_y}{dt} = -\frac{\partial H_x}{\partial z}, \quad D_z = 0,$$

or

$$(H_x, H_y) = q (E_y, -E_x)$$

$$(D_x, D_y) = q (-H_y, H_x)$$

$$= q^2 (E_x, E_y).$$

Now the equation (2) gives at once

$$E_x(1+\alpha) - i \frac{\beta n q}{c} E_y = \alpha D_x - i \frac{n q \beta}{c} D_y,$$

and

$$E_y(1+\alpha) + i \frac{\beta n q}{c} E_x = \alpha D_y + i \frac{n q \beta}{c} D_x,$$

or

$$E_x \{1 + \alpha(1 - q^2)\} - i \frac{n q \beta}{c} (1 - q^2) E_y = 0,$$

$$E_y \{1 + \alpha(1 - q^2)\} + i \frac{n q \beta}{c} (1 - q^2) E_x = 0,$$

which are equivalent to the two equations

$$(E_x + i E_y) \left[ (q^2 - 1) \left( \alpha - \frac{\beta n q}{c} \right) - 1 \right] = 0,$$

$$(E_x - i E_y) \left[ (q^2 - 1) \left( \alpha + \frac{\beta n q}{c} \right) - 1 \right] = 0.$$

These equations can be satisfied in two ways:

(1) Either by

$$E_x + i E_y = 0 \quad \text{and} \quad (q^2 - 1) \left( \alpha + \frac{\beta n q}{c} \right) - 1 = 0,$$

(2) or by

$$E_x - i E_y = 0 \quad \text{and} \quad (q^2 - 1) \left( \alpha - \frac{\beta n q}{c} \right) - 1 = 0.$$

Now examine what this means: let  $q_1$  and  $q_2$  be the respective roots of the two cubics in (1) and (2), and consider the propagation of a beam of light which starts with the electric force polarized in the plane of the axis of  $y$  and with an amplitude  $E$

$$E_x = E e^{int}, \quad E_y = 0.$$

The medium splits this beam into two oppositely circularly polarized beams, in the one of which

$$E_{x_1} = \frac{1}{2} E e^{int}, \quad E_{y_1} = -\frac{i}{2} E e^{int}$$

initially, and in the other

$$E_{x_2} = \frac{1}{2} E e^{int}, \quad E_{y_2} = \frac{i}{2} E e^{int}.$$

The first of these beams, in which  $E_{x_1} + i E_{y_1} = 0$ , is propagated through the medium with a velocity equal to the real part

of  $\frac{c}{q_1}$ ; while the second, in which  $E_{x_2} - iE_{y_2} = 0$ , is propagated with a velocity equal to the real part of  $\frac{c}{q_2}$ . The result is that at a depth  $z$  into the medium from the place of entry of this beam the amplitudes in the respective components are

$$E_{x_1} = \frac{1}{2} E e^{in(t - \frac{q_1 z}{c})}, \quad E_{y_1} = -\frac{iE}{2} e^{in(t - \frac{q_1 z}{c})},$$

and 
$$E_{x_2} = \frac{1}{2} E e^{in(t - \frac{q_2 z}{c})}, \quad E_{y_2} = \frac{iE}{2} e^{in(t - \frac{q_2 z}{c})},$$

so that in all

$$E_x = \frac{E}{2} \left( e^{in(t - \frac{q_1 z}{c})} + e^{in(t - \frac{q_2 z}{c})} \right),$$

and 
$$E_y = -\frac{iE}{2} \left( e^{in(t - \frac{q_1 z}{c})} - e^{in(t - \frac{q_2 z}{c})} \right),$$

and therefore

$$\begin{aligned} \frac{E_y}{E_x} &= +i \frac{e^{-in \frac{q_2 z}{c}} + e^{-in \frac{q_1 z}{c}}}{e^{-in \frac{q_2 z}{c}} - e^{-in \frac{q_1 z}{c}}}, \\ &= \tan \left( \frac{q_1 - q_2}{2c} n z \right). \end{aligned}$$

This shows that, if the imaginary parts of  $q_1$  and  $q_2$  are the same, then the beam of light is still plane polarized even at this depth, but the plane of polarization has been turned through an angle

$$\frac{nz}{2c} (q_1 - q_2).$$

This is the case when the absorption of the two beams is the same, which in reality only occurs when there is no absorption at all. In every other case the light is elliptically polarized, but the rule of rotation of the major axis is always very approximately determined by the real part of  $(q_1 - q_2)$ . We need not here enter further into the details of this analysis, which are fully dealt with in most text-books\*. In any case the complete circumstances are determined when we know  $(q_1 - q_2)$  and can effect its separation into real and imaginary parts.

\* See for example Voigt, 'Magneto- u. Elektro-optik,' pp. 32-34.



Although the equations for  $q_1$  and  $q_2$  could be solved absolutely this process appears unnecessary, as the restrictions imposed by the fundamental assumptions are probably such as could not stand the test of absolute accuracy. Besides the approximation obtained by treating  $\beta$  as small is a very good one, and would be sufficiently justified in most cases. The equations are

$$(q^2 - 1) \left( \alpha \pm \frac{\beta n q}{c} \right) = 1,$$

and if we expand  $q$  in powers of  $\beta$  we get

$$\left. \begin{matrix} q_1 \\ q_2 \end{matrix} \right\} = q_0 \pm \frac{1}{2} \frac{\beta n}{c \alpha^2} + A \beta^2 + \dots;$$

so that

$$q_1 - q_2 = \frac{\beta n}{c \alpha^2}$$

to a very good approximation if  $\beta$  is small. Substituting the values for  $\alpha$  and  $\beta$  we find

$$\frac{c}{n} (q_1 - q_2) = \frac{\left( \sum' \frac{be^2/m}{n_r^2 + inn_r' - n^2} \right) \left( \sum \frac{e^2/m}{n_r^2 + inn_r' - n^2} \right)}{\left( 1 - \sum \frac{ae^2/m}{n_r^2 + inn_r' - n^2} \right)^2},$$

and this is the general formula from which all the circumstances of the phenomena are obtained.

In regions of the spectrum where there is no appreciable absorption, the imaginary parts of these formulæ are negligibly small, and then the difference  $\frac{n}{2c} (q_1 - q_2)$  represents the rate of rotation of the plane of polarization in the substance, usually called  $\omega$ , so that under these circumstances

$$\frac{2c^2 \omega}{n^2} = \frac{\left( \sum' \frac{be^2/m}{n_r^2 - n^2} \right) \left( \sum \frac{be^2/m}{n_r^2 - n^2} \right)}{\left( 1 - \sum \frac{ae^2/m}{n_r^2 - n^2} \right)^2},$$

a formula which can be adopted into an explanation of most of the apparent anomalies in the polarimetric behaviour of solutions when their aggregate constitution is varied. It leads for instance, under the usual assumptions that

$\sum \frac{e^2/m}{n_r^2 - n^2}$  taken per unit volume for any definite set of electrons is proportional to the partial density of the substance with whose molecules they are associated, to a formula

for the rotative power of a mixture containing different active substances at partial densities  $\rho_1, \rho_2, \dots$  and inactive substances at partial densities  $\sigma_1, \sigma_2, \dots$  which is of the form

$$\frac{2\omega}{n^2} = (r_1' \rho_1 + r_2' \rho_2 + \dots) \frac{n_1 \rho_1 + n_2 \rho_2 + \dots s_1 \sigma_1 + s_2 \sigma_2 + \dots}{[1 - a(n_1 \rho_1 + n_2 \rho_2 + \dots s_1 \sigma_1 + s_2 \sigma_2 + \dots)]^2},$$

wherein  $r_1', r_2', \dots; n_1, n_2, \dots; s_1, s_2, \dots$  are all physical constants of the respective substances to which they refer, depending on the nature of these substances and the frequency of the light.

A more fundamental interpretation of the formula, which would avoid any irregularity in the probable truth of the above assumption, makes it depend on the mean index of refraction of the medium ( $\epsilon$ ) which we know is determined by the relation

$$\frac{\epsilon^2 - 1}{1 + a(\epsilon^2 - 1)} = \sum \frac{e^2/m}{n_r^2 - n^2},$$

and thus

$$\frac{2c^2\omega}{n^2} = \left( \sum' \frac{be^2/m}{n_r^2 - n^2} \right) (\epsilon^2 - 1) (a\epsilon^2 - 1 + 1).$$

It would appear that the main cause of the variation of  $\omega$  is identical with that which causes the variation of  $\epsilon$ , a fact on which it is necessary to insist.

One or two fundamental difficulties occur, however, even in the applications of this formula. Some of these have already been mentioned in a previous connexion (*l. c.*); another one is that it would indicate no change in the sign of the rotation on passage across an absorbing region, a phenomenon observed by Cotton. Closer investigation to which we shall now proceed will, however, remove even these discrepancies.

In the neighbourhood of the spectrum near an absorption band, the absorption determined by the imaginary parts of  $q_1$  and  $q_2$  is no longer negligible; but even in these cases it is only the absorption due to the electrons giving rise to the one near band that is appreciable and needs to be reckoned with. Two cases may, however, present themselves, the band may arise from a set of the rotationally active electrons or from a group of the others. The latter case being the simpler is treated first. If we write

$$q_1 - q_2 = \frac{2c}{n} (\omega - i\omega'),$$

then  $\omega$  determines the relative velocities of the two beams

(and approximately the rate of rotation of the polarization plane), and  $\omega'$  their relative absorption, the two quantities alone necessary to determine the nature of the emergent light. We have now

$$\frac{2c^2}{n^2}(\omega - i\omega') = \frac{B\left(A_1 + \frac{N_1 e^2/m}{n_1^2 - n^2 + inn_1'}\right)}{\left(1 - aA_1 - \frac{aN_1 e^2/m}{n_1^2 - n^2 + inn_1'}\right)^2}$$

wherein  $N_1$  is the number of electrons per unit volume with free period  $n_1$ , which are responsible for the band under consideration ;

$$A_1 = \sum \frac{e^2/m}{n_r^2 - n^2},$$

this sum being taken per unit volume over all the electrons in the medium other than those reckoned in  $N_1$ ; and finally,

$$B = \sum' \frac{be^2/m}{n_r^2 - n^2},$$

this sum being taken only over the rotationally active electrons for none of which is  $n_r = n_1$ .

We can again interpret this formula in terms of the mean index of refraction  $\epsilon$  and mean absorption coefficient  $\kappa$  determined as usual by

$$\frac{(\epsilon - i\kappa)^2}{1 + a(\epsilon - i\kappa)^2} = A_1 + \sum \frac{N_1 e^2/m}{n_r^2 - n^2 + inn_1'}.$$

The result is that

$$\begin{aligned} \frac{2c^2}{n^2}(\omega - i\omega') &= B[\{(\epsilon - i\kappa)^2 - 1\}\{a(\epsilon - i\kappa)^2 + 1 - a\}] \\ &= B[(\epsilon^2 - \kappa^2 - 1 - 2i\epsilon\kappa)\{a(\epsilon^2 - \kappa^2 - 1) + 1 - 2ia\epsilon\kappa\}], \end{aligned}$$

so that

$$\frac{2c^2\omega}{n^2} = B[(\epsilon^2 - \kappa^2 - 1)\{a(\epsilon^2 - \kappa^2 - 1) + 1\} - 4a\epsilon^2\kappa^2]$$

$$\frac{2c^2\omega'}{n^2} = 2B[(a+1)(\epsilon^2 - \kappa^2 - 1) + 1]\epsilon\kappa.$$

To discuss these formulæ it will be convenient to resolve them by a method similar to that adopted by the author in a recent communication\* on absorption spectra. The formulæ

\* 'Ueber die Veränderlichkeit von Absorptionsspektren,' *Phys. Zeitsch.* xiv. pp. 841-844 (1913).

are in fact simplified by writing

$$x_1^2 = n_1^2 - \frac{\alpha \rho_1}{1 - \alpha A_1}, \quad \rho_1 = \frac{N_1 e^2}{m}, \quad \epsilon_1^2 = \frac{1 + (1 - \alpha) A_1}{1 - \alpha A_1},$$

$$2d = \frac{(1 - \alpha) \rho_1}{1 + (1 - \alpha) A_1} + \frac{\alpha \rho_1}{1 - \alpha A_1}, \quad n^2 = x_1^2 + f \tan \theta,$$

$$f = x_1 n_1' \quad \text{and} \quad d = \alpha f,$$

and neglecting the term  $\alpha n'^2$  in comparison with the term  $x_1^2 n'^2$ , which always accompanies it. We have then

$$\frac{2\epsilon^2}{\epsilon_1^2} = L + M, \quad \frac{2\kappa^2}{\epsilon_1^2} = L - M,$$

$$\text{where} \quad L^2 = 1 + 2\alpha^2 - 2\alpha \sin 2\theta + 2\alpha^2 \cos 2\theta$$

$$M = 1 - \alpha \sin 2\theta,$$

so that

$$\epsilon^2 \kappa^2 = \epsilon_1^4 \frac{(L^2 - M^2)}{4} = \alpha^2 \epsilon_1^4 \cos^4 \theta$$

$$\epsilon^2 - \kappa^2 = \epsilon_1^2 M = \epsilon_1^2 (1 - \alpha \sin 2\theta).$$

We have therefore

$$\frac{2c^2 \omega}{Bn^2} = \left\{ (\epsilon_1^2 - 1) - \alpha \epsilon_1^2 \sin 2\theta \right\} \left\{ a(\epsilon_1^2 - 1) + 1 - \alpha \alpha \epsilon_1^2 \sin 2\theta \right\}$$

$$- 4\alpha^2 \epsilon_1^2 \cos^4 \theta$$

$$= \frac{2c^2 \omega_1}{Bn^2} - \{2a(\epsilon_1^2 - 1) + 1\} \alpha \epsilon_1^2 \sin 2\theta$$

$$- \alpha \epsilon_1^4 \alpha^2 (1 + 2 \cos 2\theta + \cos 4\theta),$$

where

$$\frac{2c^2 \omega_1}{Bn^2} = (\epsilon_1^2 - 1) \{a(\epsilon_1^2 - 1) + 1\}.$$

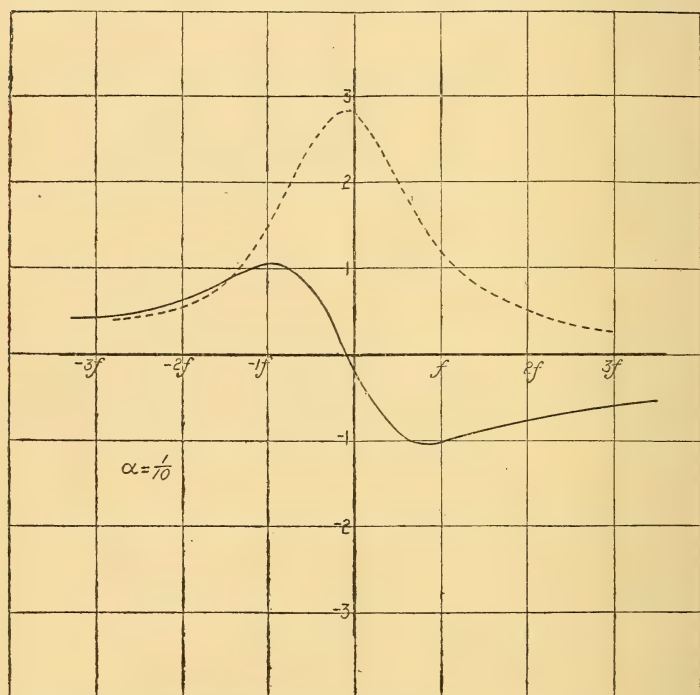
$$\text{Also} \quad \frac{2c^2 \omega'}{Bn^2} = 2\alpha \epsilon_1^2 \cos^2 \theta [(a + 1)\epsilon_1^2 - a - (a + 1)\alpha \epsilon_1^2 \sin 2\theta].$$

These formulæ for  $\omega$  and  $\omega'$  are suitable for the estimation of the disturbance in the otherwise uniform course of the rotatory dispersion due to the presence of absorption bands of varying intensity. In order to illustrate the general nature of the effects in a particular case, I have plotted on diagrams the values of the functions  $\frac{6c^2}{Bn^2}(\omega - \omega_1)$  and  $\frac{6c^2 \omega'}{Bn^2}$  against  $x (= n^2 - x_1^2)$  for the values 0.1 (fig. 1), 1 (fig. 2), and 10 (fig. 3) of the constant  $\alpha$ , which depends essentially on the



density of the electrons exciting the band under consideration. The particular case chosen is that for which  $\epsilon_1^2 = 2$  and  $a = 1/3$ ; the dotted lines represent the curves for  $\frac{6c^2\omega'}{Bn^2}$ , and the continuous ones the other function. In figures 2 and 3 the maxima of  $\frac{6c^2\omega'}{Bn^2}$ , which are not exhibited, are respectively 28 and 2800.

Fig. 1.

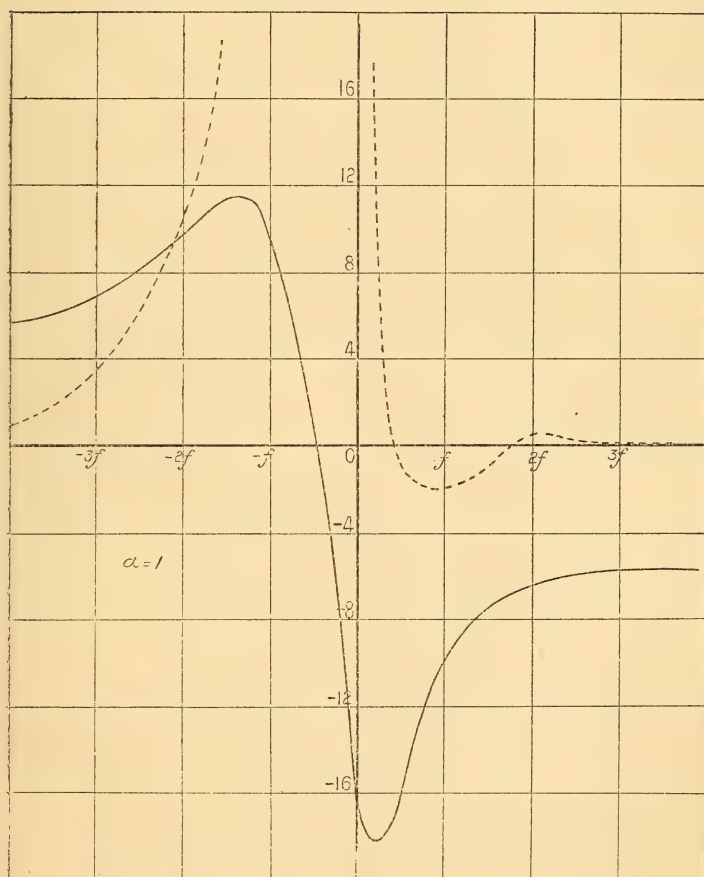


The lowest point of the continuous curve always occurs for a positive value of  $x < \sqrt{3}f$ , and the maximum point of the dotted curve for a negative value of  $x$  between 0 and  $-\frac{1}{\sqrt{3}}f$ .

These diagrams illustrate very vividly the important characteristics of the phenomena. The presence of the absorption band in general causes an increase in the rotation on its more refrangible side and a decrease on the other side, even to a reversal in sign. The decrease is in general much

more pronounced than the increase except when the density of the absorbing molecules is small, when there is approximate symmetry. This is in complete agreement with the experimental results obtained by Cotton.

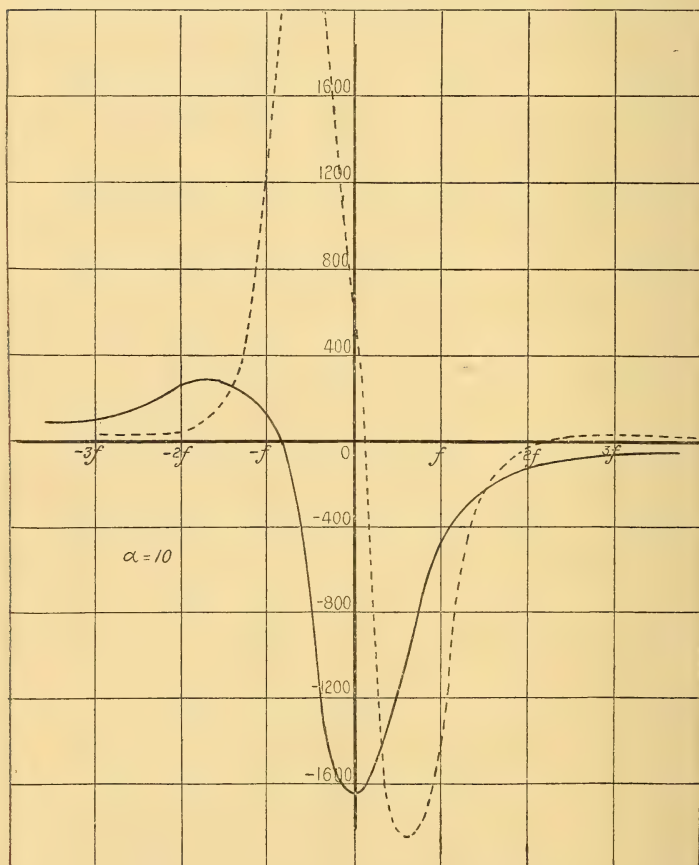
Fig. 2.



The relative absorption of the two rays is also increased in the neighbourhood of the band, where it in fact changes very rapidly. For small densities it is symmetrical on both sides of the band, but for larger densities it may be of opposite sign on the two sides. This would indicate opposite elliptical polarization of a beam of light, according as its frequency is just below or just above that of the absorption band.

Another important point to be noticed is that the effects here described always accompany an absorption band of the type specified. But we have already seen\* how the position of the absorption band of a substance varies not only as a

Fig. 3.



consequence of a variation in the state of aggregation of the substance itself, but also as a result of mixing other substances with it. Thus variations in the conditions of the rotating substances will result in a variation in the position of the spectrum in which the above characteristics present themselves. This may contain an explanation of the difficulty

\* Cf. Livens, 'Ueber die Veränderlichkeit von Absorptionsspektren,' i., ii., iii. *Phys. Zeitsch.* xiv. (1913).

inherent in the simpler formula, obtained by neglecting the absorption, which did not admit a minimum rotation\* until a change in the sign of the rotation had taken place. In fact changing the concentration of the solution may conceivably bring into closer proximity an absorption band, and complications are at once introduced which may very well explain the results actually obtained. I have not sufficient details to hand to tell whether this explanation is a valid one in the few cases involved, but the matter could easily be tested. A similar explanation applies to the other difficulty (*l. c.*) mentioned, viz. that the minimum rotation of a substance in solution, for changing concentration, is independent of the solvent.

Several other deductions could be made immediately from the above formula, but no advantage is thereby gained owing to the lack of experimental results on this subject, with which they can be compared. Several obvious tests of the theory, however, at once present themselves, and could be submitted to examination. For the present we may be content with the above explanations, and may therefore proceed to an examination of the more general formula in the remaining case of any importance, viz. when the absorption which is taken into account arises from a group of rotationally active electrons. This formula in this case can be written, in the same notation,

$$\frac{2^2}{n^2}(\omega - i\omega') = \frac{\left(B_1 + \frac{N_1 b e^2 / m}{n_1^2 - n^2 + i n n_1'}\right) \left(A_1 + \frac{N_1 e^2 / m}{n_1^2 - n^2 + i n n_1'}\right)}{1 - aA - \left(\frac{a N_1 e^2 / m}{n_1^2 - n^2 + i n n_1'}\right)^2}.$$

The calculations and discussions for this formula can be made to depend on those already given in the simpler case above. In fact if we define  $\omega_1$  and  $\omega_1'$  by the relation

$$\frac{2c^2}{n^2}(\omega_1 - i\omega_1') = \frac{B_1 \left(A_1 + \frac{N_1 e^2 / m}{n_1^2 - n^2 + i n n_1'}\right)}{\left(1 - aA_1 - \frac{a N_1 e^2 / m}{n_1^2 - n^2 + i n n_1'}\right)^2}.$$

then they are susceptible of the same treatment as  $\omega$  and  $\omega'$  above; but then

$$\omega - i\omega' = \left(1 + \frac{N_1 b e^2}{m B_1} \cdot \frac{1}{n_1^2 - n^2 + i n n_1'}\right) (\omega_1 - i\omega_1'),$$

so that  $\omega$  and  $\omega'$  are easily determined. We need not enter

\* See Phil. Mag. June 1913.



further into the results here. It is, however, worth noticing that in this case no change of sign of the rotation can take place on crossing the absorption band: this is the essential difference between the two cases. The conclusion is, however, precisely the opposite of that drawn from Drude's theory; in fact on that theory the change of sign in the rotation takes place only when an absorption band due to chirally active electrons is crossed.

The general formulæ thus obtained, although rather complicated, are nevertheless sufficiently general to contain an effective explanation of all of the apparent anomalies in the behaviour of the intrinsic optical rotatory power of isotropic media. This theory, which makes the rotative power depend essentially on the ordinary dispersion and absorption in the medium, would indicate large variations of this rotative power consequent on any variation of condition which alters to any appreciable extent the usual dispersive and absorptive properties of the medium.

Of course it may be that the present theory is not general enough to include all the details of a very complex phenomena: this can only be tested by experiment. It appears, however, to be of far more general applicability than any other theory of the phenomena yet proposed, and is therefore deserving of a strict experimental examination to test its completeness, before other assumptions are adopted to explain what at first sight appear to be anomalies in the phenomena, but which are all, or nearly all, probably involved in some simple physical theory of the subject such as that developed above.

Sheffield, Feb. 4, 1914.

*Note added April 22nd, 1914.*—Since writing the above it has been pointed out to me that the assumption  $B=H$  is not valid in the present connexion. This appears to have been noticed first by Voigt (*Ann. der Physik*, lxi. p. 307, 1899) who finds that, in order that the equations of the theory may conform to the energy principle in its usual form, it is necessary to put

$$B=H-\frac{\beta}{\alpha c} \frac{dP}{dt}$$

if terms in  $\beta^2$  and higher powers are neglected.

It is therefore necessary to modify the form of the

fundamental equations (1) given above to

$$-\frac{1}{c} \frac{dH_x}{dt} + \frac{\beta}{\alpha c^2} \frac{d^2 P_x}{dt^2} = \frac{\partial E_y}{\partial z}, \quad -\frac{1}{c} \frac{dH_y}{dt} + \frac{\beta}{\alpha c^2} \frac{d^2 P_y}{dt^2} = -\frac{\partial E_x}{\partial z}, \quad H_x = 0;$$

and 
$$\frac{1}{c} \frac{dD_x}{dt} = \frac{\partial H_y}{\partial z}, \quad \frac{1}{c} \frac{dD_y}{dt} = -\frac{\partial H_x}{\partial z}, \quad D_z = 0.$$

Under the conditions above specified these equations are equivalent to the two relations

$$(E_x \pm iE_y)(q^2 - 1) = (P_x \pm iP_y) \left(1 \mp \frac{q\beta n}{\alpha c}\right).$$

But we still have from equation (2) as above

$$(E_x \pm iE_y) = \left(\alpha \pm \frac{q\beta n}{c}\right) (P_x \pm iP_y),$$

so that the equations for  $q$  are now

$$\alpha(q^2 - 1) \left(1 \pm \frac{iq\beta n}{c}\right)^2 = 0,$$

which, to the first order in  $\beta$ , are the same as

$$(q^2 - 1) \left(\alpha \pm \frac{2\beta n q}{c}\right) = 0,$$

which are the same as in the text with  $2\beta$  instead of  $\beta$ . The final formula for the rotation of the plane of polarization is therefore exactly double that given in the text. G. H. L.

## CVII. The Magneto-optics of Iodine Vapour.

By R. W. WOOD and G. RIBAUD\*.

THE magnetic rotatory polarization of iodine vapour was discovered in 1906 by one of the present writers †.

A small glass bulb, highly exhausted and containing a small crystal of iodine, was placed between the perforated pole-pieces of a powerful electromagnet, and warmed until the iodine vapour showed a light purple tint. Polarized white light was now passed through the hollow cores of the magnet and the bulb, and received by a Nicol's prism set for the position of extinction. On exciting the magnet the nicol transmitted light of a bright emerald-green colour, as a result of the selective rotation of vapour due to the presence of

\* Communicated by the Authors.

† R. W. Wood, Phil. Mag. xii. p. 329 (1906).

innumerable absorption lines in the yellow, green, and blue region of the spectrum. By means of a concave grating of 14 feet radius, the spectrum of the transmitted light was resolved into bright lines, equalling in narrowness the emission lines of the iron arc. Similar results were obtained with the vapour of sodium \* and bromine †, and the spectra obtained in this way were named magnetic rotation spectra.

In the case of the vapour of sodium it was found that in the red and orange region, some of the absorption lines rotated the plane of polarization to the right, others to the left. This phenomenon was observed by employing a double prism of Fresnel (right and left handed quartz), which, when employed in the well-known manner of Macaluso and Corbino, causes the appearance of horizontal dark bands in the spectrum.

Selective rotation of the medium manifests itself by the penetration of light from the bright into the dark bands. In the red and orange region, bright needles of light were observed to shoot into the dark region as soon as the magnet was excited, some of them projecting themselves downward, others upward, indicating positive and negative rotations of the plane of polarization.

In the green and blue regions of the spectrum, the rotations, while sufficient to give a brilliant bright line spectrum, were insufficient to make observations with the double prism possible. It must be remembered that a rotation of  $90^\circ$  is necessary to cause the light to pass from the centre of a bright band to the centre of a dark one. In the case of both sodium and iodine comparatively few of the absorption lines, of which there are many thousand, appeared to rotate the plane of polarization to an appreciable degree, the magnetic rotation spectrum being made up of something over 100 lines altogether. In the case of bromine, observations made with a concave grating of 1.60 m. focal length (when used with a collimating lens) have shown bright lines (rotation lines) for all of the absorption lines which the grating was capable of resolving, in other words the absorption spectrum and the magnetic rotation spectrum were complementary. This was, however, only true when the vapour was at very low density. At higher densities the appearances were totally different.

Recent work on the resonance spectra of iodine has shown that a resolving power of at least 300,000 is necessary for an exact study of the phenomena produced by all of

\* R. W. Wood, *Phil. Mag.* xii. p. 499 (1906).

† G. Ribaud, *C. R.* clv. p. 900 (1912).

the rays of absorption, which are extremely fine and very close together, over one hundred having been counted in region 6 Å. U. in width (distance between the D lines), on a photograph made with the 42-foot plane grating spectrograph at East Hampton, N.Y.

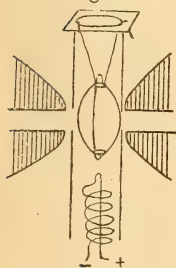
The remarkable resonance spectra excited when the vapour is stimulated by monochromatic light of a frequency corresponding to that of one of these very fine absorption lines, have shown the importance of a study of the vapour in a magnetic field with a resolving power sufficient to clearly separate all of the lines.

The aim of the present investigation has been to determine the exact nature of the rotation produced by the lines of absorption, since the more recent investigations, just alluded to, have shown that the earlier results dealt with rotations produced by close groups of lines, no record having been obtained of the nature of the rotation to the right and left of a single line.

It was of especial importance to determine whether the rotation to the right and left of an absorption line was of the same nature, *i.e.* either positive or negative, as is the case with the D lines of sodium, or whether any case of anomalous rotation occurred, *i.e.* positive on one side of the line and negative on the other.

Small glass bulbs about 2.5 cm. in diameter, highly exhausted and containing a crystal of iodine, were mounted between the poles of a large Weiss electromagnet. The bulbs were supported in a brass tube of 3 cm. internal diameter, furnished with two lateral holes for the passage of the light, and heated electrically by a spiral of nickel wire placed below the bulb. A cover of mica forced the heated air rising around the bulb to escape through the side holes, and prevented iodine crystals from depositing on the walls in the path of the beam of light, as was invariably the case if the brass tube was open at the top. The source of light was a quartz mercury arc arranged "end on," the observations being restricted to the seven or more absorption lines of iodine which are covered by the broadened green mercury line.

Fig. 1.



Our first observations were made with a six-inch plane grating in the fourth order spectrum (res. power 300,000) combined with a plano-convex lens of 4.20 m. focus. This lens was kindly placed at our disposal by M. Deslandres, director of the Meudon Observatory.



It was hoped that observations could be made with the Fresnel double prism, but preliminary experiments showed that the rotations were too small to cause any appreciable penetration of light into the region of the dark bands. It was necessary, therefore, to make use of the method previously used in the study of the magnetic rotation of sodium in the green region of the spectrum. The polarizing nicol is rotated until sufficient light is restored to render the absorption lines visible (10 to 15 degrees). The magnet is then excited and the spectrum brightens at the points where the rotation is in the opposite direction to that in which the nicol has been rotated, and darkens where the rotation is in the same direction.

Suppose that the rotation is positive to right and left of one absorption line, and negative to the right and left of another. The former will appear narrower when the field is excited as a result of the brightening of the edges of the dark line. The latter will, however, appear broader than in the absence of the magnetic field. If the rotation is anomalous, the centre of the absorption line will appear slightly shifted as a result of its becoming brighter on one side and darker on the other. This method of observation gives results quite as conclusive as those obtained with the Fresnel prisms, and is well adapted to cases where the maximum rotation is less than forty or fifty degrees.

It was found necessary to orient the analysing nicol so as to obtain the maximum reflexion from the grating, for the polarizing power of a grating is very large, especially in spectra of higher orders than the second. In the present instance the difference in the reflecting power was certainly five or six fold for vibrations parallel and perpendicular to the grooves. With this arrangement of the apparatus we had no difficulty in observing rotations both positive and negative in direction, but the intensity of light was not quite sufficient to enable us to be sure of what happened on both sides of the lines. The rotation appeared to be more marked on one side of the lines than on the other, and we felt uncertain about our results.

We accordingly substituted for the grating a very fine echelon, loaned through the kindness of Mr. F. Twyman, of the Hilger Company. This instrument consisted of 20 plates in optical contact (each plate 15 mm. thick), and gave a resolution equal or superior to that of the grating and an image of much greater intensity.

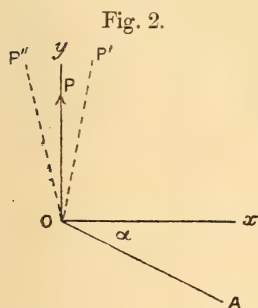
It was immediately obvious, with this instrument, that certain lines became broader when the magnet was excited,

and that a reversal of the direction of the field caused them to become so fine as to be almost invisible, as a result of the brightening of the regions bordering them. This brightening was in some cases much stronger on one side of the line than on the other.

To obviate the necessity of reversing the field to observe these changes, a half-wave plate of mica was placed over one half of the slit of the collimator, the principal directions of the plate coinciding with those of the polarizing prism. As the echelon showed a trace of astigmatism, it was necessary to form an image of the edge of the half-wave plate at a distance of a few millimetres behind the slit, in order to have a sharp hair-line divide the two fields of view.

The action of the half-wave plate is as follows:—

Let OP (fig. 2) represent the direction of vibration of the light traversing the iodine bulb. The principal directions of the mica plate  $oy$  and  $ox$  being parallel and perpendicular respectively to OP, the light traverses the plate without change. The analysing nicol is now turned through an angle  $\alpha$  from the position of extinction, and it transmits the component of OP parallel to OA.

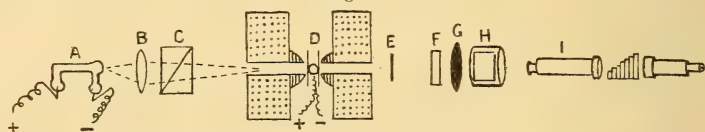


Suppose now that a certain wave-length  $\lambda$  is rotated by the magnetized iodine vapour from the position OP

to OP', *i. e.* in the same direction as that in which the analyser was turned. In that part of the field of vision given by the light which has not traversed the mica, the wave-length  $\lambda$  will appear darker than before the excitation of the magnet. The vibration which traverses the mica (wave-length  $\lambda$ ) is rotated by the mica from the position OP' to OP'', and is consequently more copiously transmitted by the analyser than the wave-lengths not rotated by the iodine. Consequently  $\lambda$  appears brighter in this part of the field of vision. The two conditions seen with magnetic fields of opposite direction are thus visible simultaneously one above the other, and in exact coincidence. Any shift, due to anomalous rotation, would thus be doubled, but no such shift was observed. The arrangement of the entire apparatus is shown in fig. 3. It was at once evident that the observation of a larger rotation on one side of certain absorption lines than on the other, made with the grating, was a correct one; and the explanation of the phenomenon was apparent as soon as a careful study of the rotation produced by the various lines had been made.

The absorption lines which we have investigated are numbered, 2, 3, 4, 4', 5 and 6. These numbers conform to

Fig. 3.

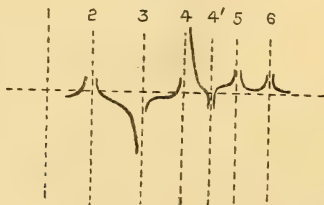


- A. Mercury arc.
- B. Lens forming image of arc on bulb at D.
- C. Polarizing prism.
- E. Half-wave plate.
- F. Cell of bichromate of potash and neodymium to remove yellow and violet lines.
- G. Lens forming image of E 3 mm. inside the slit of collimator I.
- H. Analysing nicol.

those used in previous papers on the resonance spectra. The line 4' is much weaker than the others, and did not record itself on the earlier photographs made with vapour less dense than that used in the present case.

The curves of rotation for these lines are shown by fig. 4 : they are only roughly quantitative.

Fig. 4.



The direction of the rotation by the absorption line No. 4 is the same as for the D lines of sodium.

In this group of lines the direction of the rotation changes as we pass from line to line, which explains perfectly why the angular magnitude of the rotation is so small in comparison with that exhibited by the D lines. The + rotation due to a given line is nearly neutralized by the - rotations of its two neighbours. We also see at once why the rotation on one side of a line may be much greater than on the other. For example, we have very strong rotation to the right of line 4 since the opposed rotation due to the faint line 4' is very small, and the effect contributed by the next line 5 is of the same sign. The rotation to the left of 4 is, however, very small since line 3, with its opposite rotation, lies very close to 4. In the case of line 3 the strong rotation is to

the left, since the distance between 2 and 3 is greater than the distance between 3 and 4.

It is very probable that the same condition holds for the vapour of sodium, at least in the green region. In the red and orange portion of the spectrum it is probable that the + and - rotations observed with the Fresnel double prism were due to close groups of lines with rotations of the same sign. It was observed that the luminous needles which penetrated the dark bands were almost invariably found on one side or the other of broad absorption lines, which were undoubtedly unresolved groups of fine lines. Suppose we have a group of a dozen lines, the first four rotating the plane of polarization in the same direction, while for the remainder the sign changes in passing from line to line. It is clear that if the spectroscope does not resolve the lines the Fresnel prism will show a strong rotation in the vicinity of the first lines, that is on one side of the group, and no rotation at all on the other; in other words, we apparently have a broad line which shows rotatory power on one side only, which was exactly what was found in the earlier work with sodium.

#### *Examination for the Zeeman Effect.*

Since the selective rotatory power of the vapour in the vicinity of absorption lines can be explained by a longitudinal Zeeman effect, it was of interest to see whether, with the high resolving power at our disposal, any evidence of such an effect could be observed.

We used for the purpose an arrangement employed by one of us in a similar investigation of the vapour of bromine.

A double circular analyser (two  $\lambda/4$  plates of mica, one rotated through  $90^\circ$  with respect to the other) was mounted between the iodine bulb and the analysing nicol (azimuth  $45^\circ$  with respect to the neutral lines of the plates). One obtains in this way two fields of view separated by a fine line, one corresponding to right-handed, the other to left-handed vibrations.

If a longitudinal Zeeman effect exists, the absorption line, which runs across both fields of view as a continuous line in the absence of the magnetic field, should be displaced in opposite directions in the two fields as soon as the magnet is excited. We were, however, unable to detect a trace of such a shift in the case of any of the iodine lines.

Since the absorption lines 3 and 4 are separated by a distance of about  $\frac{1}{20}$  Å. U. we should have certainly been able to detect a shift of 0.01 Å. U.

From this we must suppose, that if the Zeeman effect exists, it is less than 0.01 Å. U. for a field of 20,000 gauss.



*Re-establishment of light perpendicular to lines of force.*

Cotton has shown that if a sodium flame is placed in a magnetic field, between crossed nicols, the light traversing it in a direction perpendicular to the lines of force is re-established in the vicinity of the D lines, if the planes of the nicols are at  $45^\circ$  with the lines of force. The same phenomenon has been observed by one of us in the case of the non-luminous vapour of metallic sodium.

Voigt and Wiechert have studied the spectrum composition of this re-established light under high dispersion, and have given a theoretical treatment based upon the marked Zeeman effect shown by the lines.

The same experiment has been tried by Cotton with iodine vapour, and by one of us with bromine vapour, with a more powerful field, with negative results.

We have, however, obtained a very marked restitution of light, employing the iodine bulb used in the previous experiments, which was unfortunately too feeble to permit of its examination with the echelon. With the crater of the carbon arc as a source the restored light was quite brilliant, and of the same emerald-green colour as in the longitudinal experiment.

*Destruction of Fluorescence by Magnetic Field.*

Steubing\* has observed a diminution of the intensity of iodine vapour fluorescence in a magnetic field amounting to as much as 30 per cent. We have repeated the experiment with a much more powerful field and have succeeded in almost completely abolishing the fluorescence.

The effect of the magnetic field in reducing the intensity of the fluorescence becomes more marked as the vapour-pressure of the iodine is diminished.

We found that the form of tube best suited to the study of the phenomenon was as shown in fig. 5.

A thin-walled tube as free as possible from striæ, and 8 mm. external diameter, is blown out at one end into a small bulb. The tube is highly exhausted and sealed, a crystal of iodine having been introduced before drawing down the tube to a capillary. In exhausting iodine bulbs it is important to cool a portion of the tube leading to the pump with solid  $\text{CO}_2$ , to prevent the vapour of iodine from entering

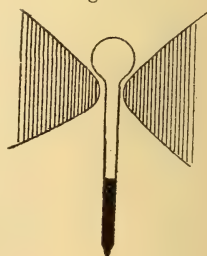


Fig. 5.

\* *Ber. Deut. phys. Ges.* 1913.

the pump. After the exhaustion is complete and the tube sealed off, the cooled portion of the tube should be cut away from the pump before the iodine vaporizes.

The tube is mounted between the pole-pieces of the magnet as shown in fig. 5, and arc or sun light concentrated at its axis with a large lens. Observations are made through the bulb, and it is advantageous to paint the lower portion with black varnish to secure a dark background. The maximum effect is obtained if the lower portion of the tube is cooled to  $0^{\circ}$  in ice. Under these conditions we estimated the reduction of intensity to amount to fully 90 per cent. with a field of 30,000 gauss, and it is probable that with a field of 50,000 the fluorescence would be practically destroyed. At a tension corresponding to room temperature, the reduction of intensity is much less, and at 35 or 40 degrees scarcely noticeable, though the fluorescence still remains fairly bright, in the absence of a magnetic field.

No obvious explanation of the effect of the field in reducing the intensity of and ultimately practically destroying the fluorescence suggests itself. We made numerous experiments to determine whether the vapour at very low pressures was thrown out of the field, but these all gave negative results. They were based for the most part upon the principle of allowing iodine to distil from a bulb at  $0^{\circ}$ , through tubes of the same size into two small bulbs cooled with solid  $\text{CO}_2$ , one tube passing through an intense magnetic field, the other well outside of it. The phenomenon may result from orientation, but we obtained no evidence of this, though we passed the light through the bulb both parallel and perpendicular to the field and observed the fluorescence in the same way.

The absorption spectrum, as we have stated, shows no change as a result of the field, but it must be remembered that our observations were made with a vapour density corresponding to 30 or 40 degrees, and the reduction in the intensity of the fluorescence is almost imperceptible at this pressure. To observe the absorption at  $0^{\circ}$  or even at room temperature, it would be necessary to observe with a larger bulb and the field would be less intense as a result.

*Conclusions.*—Up to the present the magnetic rotations of the plane of polarization in the vicinity of absorption bands may be divided into two classes. (1) Anomalous rotations, in which the sign changes in crossing the band, as observed by Cotton for certain solutions and by one of us for a solid film of a neodymium salt. Rotations of this nature appear to obtain in cases in which there is no change in the position of

the band of absorption, but merely an alteration in velocities of right and left handed circular vibrations.

(2) Rotations in which the sign is the same on opposite sides of the absorption band, as at the D lines of sodium and the iodine lines. Rotations of this type are explained by the division of the line into a Zeeman doublet by the magnetic field.

It seems probable, therefore, that there is a small Zeeman effect for the iodine, but it is doubtful if it can ever be detected as it is of the order of magnitude of the width of the lines, probably much less in fact.

The study of the magnetic rotation of the vapour of sodium by the improved methods outlined in the present paper will undoubtedly give much more satisfactory results, as the rotatory power of this vapour in the red and orange is certainly ten times as great as that of iodine.

École Normal Supérieur,  
Paris.

CVIII. *The Separate Excitation of the Centres of Emission of the D Lines of Sodium.* By R. W. WOOD and L. DUNOYER\*.

[Plate XVII. figs. 1-7.]

THE experiments of one of us on the excitation of metallic vapours by monochromatic light have shown that the centres of emission of many spectrum lines are probably in some sort of mechanical or electrical connexion. For example, the excitation of mercury vapour by the light of the cadmium spark showed that the vapour emitted the ultra-violet line of wave-length 2536 when stimulated by light of wave-length shorter than any given in the tables at the time, *i.e.* less than 2000. In the case of the resonance spectra of sodium and iodine we have innumerable examples of associated lines which spring into existence when the vapour is excited by light of frequency synchronous with one of them.

In a paper on the Resonance Radiation of Sodium Vapour, published by one of us in 1905†, it was shown that the vapour of metallic sodium in an exhausted glass tube emitted its characteristic D-line radiation when the image of a sodium flame was thrown upon it by means of a large condensing lens, a cone of yellow light marking the path of the exciting rays through the vapour. If the vapour density was increased the luminosity was restricted to "a thin skin of yellow light which lined the inner wall of the tube," owing to the failure of the exciting radiations to

\* Communicated by the Authors.

† Wood, Phil. Mag. Nov. 1905.

penetrate the vapour. Precisely similar phenomena were subsequently detected by photography in the case of mercury vapour at room temperature in a bulb of quartz excited by the mercury line 2536\*.

In the paper on the resonance of sodium vapour, it was suggested that an experiment of great interest would be to excite the vapour by the light of one sodium line only, and examine the resonance-light with a spectroscope: in this way it would be possible to determine whether the two centres of emission could be separately excited.

The experiment appeared, however, to be a difficult one to carry out, and no attempt was made at the time.

Recent improvements by one of us† in the method of carrying out the experiment enable a much brighter resonance to be obtained, and make it possible to extend observations over a period of ten or fifteen hours with a single bulb, whereas with the original apparatus the experiment was over in three or four minutes. These improvements have made it possible to carry out at last the suggested experiment on the separate excitation of the centres of emission. The device employed for the removal of  $D_1$  or  $D_2$  from the exciting beam has been recently described by one of us‡ and is an improvement of a method used in an earlier investigation of the anomalous dispersion of sodium vapour.

It is a polarization method, and may be briefly described as follows:—

If plane-polarized monochromatic light is passed through a plate of some doubly refracting crystal with its direction of vibration making an angle of  $45^\circ$  with the axis, it will emerge plane-polarized parallel to the original plane for certain thicknesses of the plate, and plane-polarized at a right angle to this plane for other thicknesses. For intermediate thicknesses it will be elliptically or circularly polarized.

If we employ a plate of quartz 30 mm. thick the emergent waves of  $D_1$  and  $D_2$  of sodium will be plane-polarized at right angles to each other, and either can be quenched by a nicol suitably oriented. If white light is used, and analysed by a spectroscope, the spectrum will be furrowed by dark bands, the distance between a bright and a dark band being, in the yellow region, 6 Ångström units, the distance between the D lines. As it is necessary to employ a large condenser and work with very divergent and convergent cones of light,

\* Wood, *Phil. Mag.* May 1912.

† Dunoyer, *Journal de Physique*, Jan. 1914.

‡ Wood, *Phil. Mag.* March 1914.

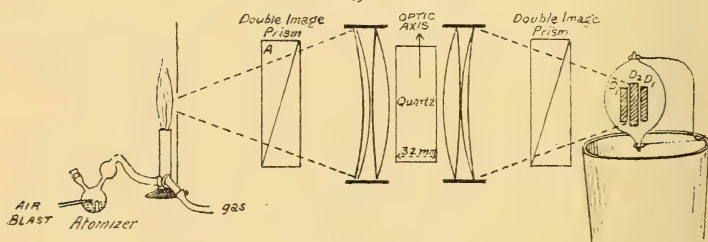


a block of quartz of very large size must be used, placed between the two halves of the condenser, since the rays which traverse the block must be parallel. If this is not the case, different pencils will traverse different thicknesses, and will be differently polarized. Moreover, one half of the light is lost at the start by the polarizing nicol. This difficulty was overcome by employing a large double-image prism, and subsequently analysing by a double-image prism. In this way, with proper orientation of the prisms, the two images containing only  $D_2$  light were superposed, the  $D_1$  images (of one half the intensity) lying to the right and left. By this expedient the  $D_2$  image had the full intensity, except for the loss by reflexion from the six transparent surfaces of the prisms and quartz block.

The quartz block used in the experiment was prepared by M. Bertin from a selected crystal of Madagascar quartz, which was previously examined by sodium light between crossed nicols to make sure that no irregularities of crystallization were present. The block measured 85 mm.  $\times$  60 mm.  $\times$  32 mm. and gave excellent results.

The arrangement of the apparatus is shown in the diagram.

Fig. 1.

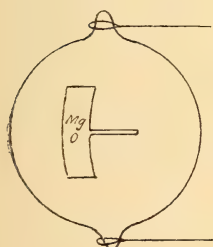


The double-image prism A is so oriented as to have the vibrations of the two transmitted beams at  $45^\circ$  with the vertical. The second double-image prism is oriented *in the absence of the quartz block*, so as to give two images of the source side by side, and separated by a distance equal to the width of each image. Each image contains both  $D_1$  and  $D_2$ . If now the quartz block is placed between the two halves of the Dunoyer condenser, all of the  $D_2$  light (for example) leaves the original images, and unites into a third image between the other two. This is the image utilized. If it is desired to have  $D_1$  light in this image, it is necessary only to rotate the block a degree or two, thereby increasing the optical path in quartz. If we rotate the analysing double-image prism the central image splits up into two, and the correct

position of the prism can be determined by bringing these two images into exact coincidence. This method obviates the 50 per cent. loss of light which results from the use of Nicol's prisms. As the double-image prisms had apertures considerably less than that of the quartz block, they were placed midway between the condenser lenses and the image and source, as shown in the figure. With prisms of too small aperture, however, placed close to the source and image, the separation of the images would be insufficient.

The source of light was a Meker burner operated by an air-blast charged with the spray of a very dilute solution of sodium chloride (a saturated solution diluted with 1000 parts of water) obtained by means of an atomizer. The burner was surrounded by an iron chimney with a vertical aperture measuring  $25 \times 5$  mm., these dimensions giving the best results with the polarizing prisms employed. The three images of the aperture, the central one of twice the brilliancy of the two lateral ones, were thrown upon the sodium bulb, which was mounted in the current of hot air rising from a large tube of fire-clay with a Meker burner at the bottom. The

Fig. 2.



sodium bulb was first coated with a deposit of magnesium oxide by holding it above a burning ribbon of the metal. The deposit was then carefully wiped off with the exception of a rectangular patch and a small horizontal strip as shown in fig. 2. This facilitated the adjustment of the polarizing separator and the spectroscope, a constant deviation instrument designed by Broca-Pellin, similar to the type now supplied by Hilger.

The bulb was rotated in its wire supports until the central band of light (the two superposed images) fell upon the strip of magnesia; the collimator of the spectroscope was pointed at the illuminated strip, and a sharp image of the latter formed on the slit by means of a small Dunoyer condenser which is free from aberration if monochromatic light is employed, as is the case in the present work.

The spectrum was now examined with an eyepiece. If both D lines were visible the quartz block was rotated until one or the other completely disappeared. It sometimes happens that only  $D_2$  appears at the top of the image, while both  $D_1$  and  $D_2$  are seen at the bottom: this results from the circumstance that, owing to the finite size of the source

of light and the consequent slight obliquity of some of the pencils, the polarizing separator distributes the monochromatic light in bands, resembling interference bands.

If the quartz plate is turned slowly the bands file across the strip of magnesia. The brighter bands represent  $D_2$ , and the feebler  $D_1$ . If the two sodium lines were of equal intensity the bands would of course be invisible.

If, now, these bands are not parallel to the strip, but cut across it obliquely, it is clear that the illumination may be by  $D_2$  at the top, by  $D_1$  and  $D_2$  at the middle, and by  $D_1$  at the bottom. In this way it would be possible to obtain, with one exposure, three types of excitation.

This method was not used, however, and the quartz block was adjusted by tipping it slightly in the direction of the source or image until the bands were vertical and the illumination constant and of the same type ( $D_2$ ) all along the slit of the spectroscope. The bulb was now rotated until the strip of magnesia fell into coincidence with one of the lateral images ( $D_1$ ), the narrow horizontal strip of magnesia cutting across the  $D_2$  image. The burner which heated the bulb was now lighted, and as soon as the superficial resonance reached its full intensity the exposure was commenced. Panchromatic plates (Wratten & Wainwright) were cut into small squares large enough to cover the eyepiece tube of the spectroscope, and were held in place against the latter by two thicknesses of black cloth and a rubber band. This method permits of very accurate focussing and is extremely convenient if the spectroscope has no plate-holder.

We first used a spectroscope furnished with cinematograph lenses of large aperture (F 4), which was loaned to us by M. Debiegne. With a Rutherford compound prism this instrument resolved the D lines on the photographic plate if the slit was made exceedingly fine. The first photograph, which was made of the resonance excited by the light of the  $D_2$  line, showed no trace of  $D_1$ . The exposure was of three hours' duration. A second attempt with a five-hour exposure showed a trace of  $D_1$ , but examination of the exciting light showed that  $D_1$  was present. This was found to be due to the rise of temperature ( $5^\circ$ ) of the room during the exposure, the polarizing separator being fairly sensitive to temperature changes. The first pictures were made before the expedient of the narrow horizontal strip of magnesia had been adopted. This proved to be a great convenience, for a record was left of the integrated condition of the exciting line for the whole exposure.



We finally substituted a large constant deviation spectrograph for the smaller instrument, as the latter barely resolved the lines, and it was often difficult to be sure of what we had on the plate.

This instrument showed very clearly that the  $D_2$  centre of emission could be set in vibration without disturbing the  $D_1$  centre, in other words we can have SODIUM VAPOUR EMITTING *one D LINE ONLY*.

Photographs made of the spectrum of the resonance radiation excited by both sodium lines (with the polarizing prisms and quartz block removed) showed that the D lines had the same intensity, in some cases  $D_1$  even appearing slightly brighter than  $D_2$ . It was found that if the amount of sodium in the flame was reduced to the least amount consistent with having resonance radiation of sufficient intensity to photograph, the  $D_2$  line came out stronger than  $D_1$  in the spectrum of the latter, as is always the case with the sodium flame. Exciting the vapour by the light of a bright soda-flame gave a resonance radiation in which  $D_1$  came out stronger than  $D_2$ , which is never the case with the flame. This is due to the circumstance that with a bright flame,  $D_2$  is more or less reversed, hence it is less effective in exciting the resonance, for the vapour in the glass bulb responds only to the wave-length forming the core of the line.  $D_1$  is less easily reversed, and may consequently be more efficient in exciting resonance.

On Pl. XVII. fig. 1, we have a photograph of the single line ( $D_2$ ) emitted by the resonating vapour, the greater intensity at the top being due to the light from the horizontal narrow strip of magnesia. Immediately below this (fig. 3) we have the two D lines as emitted by the flame. Fig. 2 shows the spectrum of the resonating vapour when excited by both sodium lines from a strong flame, and we find  $D_1$ , which is to the left, slightly brighter than  $D_2$ . In fig. 4, the resonance was excited by a feeble flame and  $D_2$  is brighter than  $D_1$ .

This change in the ratio of intensity of the two D lines of the resonance radiation leads to some curious results which were somewhat puzzling at first.

It will be remembered that the central patch of light furnished by the polarizing separator results from the superposition of two images, and, other things being equal, will have double the luminosity of the two lateral patches adjacent to it. If the light of the  $D_2$  line, which is brighter than  $D_1$  in the flame, is thrown into the central patch, we should expect it to be more than twice as bright as the lateral patches adjacent to it. It was observed, however, that the



resonance radiation from the central patch was often no brighter than that from the lateral patches which were excited by  $D_1$  light. It was found, however, that if the amount of sodium in the exciting flame was reduced, the lateral spots of resonance radiation diminished in intensity, while the central one changed scarcely at all, retaining a brilliancy of about double that of the lateral ones. This will be easily understood from what has just been said about the greater intensity of the  $D_1$  line in the resonance radiation excited by a brilliant flame.

Photographs showing this phenomenon are reproduced on Pl. XVII. figs. 5, 6, and 7. Fig. 5 is a photograph of the three patches of exciting light thrown on a bulb covered with magnesia. The central one, which contains the  $D_2$  light, is twice as bright as the lateral ones ( $D_1$ ).

In fig. 7 we have the photograph of the resonance radiation from the bulb under the same conditions of illumination. All three strips have approximately the same intensity. Fig. 6 was made under the same conditions, except that the amount of sodium which the atomizer fed to the flame was greatly reduced. Here we have practically the same intensity ratio in the case of the resonance radiation as obtains in the case of the magnesia. All of these results are easily explained by the circumstance that  $D_2$  is more easily reversed than  $D_1$ . The white spots of light in figs. 6 and 7 are due to regular reflexion from the glass walls of the bulb.

The light of the exciting flame was examined with a very powerful echelon of 20 plates in optical contact, each plate 15 mm. in thickness. This instrument was loaned by the kindness of Mr. Twyman of the Adam Hilger Co. The D lines were examined separately by interposing the polarizing separator between the flame and the instrument. It was found that  $D_2$  showed a faint trace of reversal, even with the minimum quantity of sodium in the flame.  $D_1$ , however, reversed only when the amount of sodium was considerably increased.

The resolving power of the echelon was about 300,000, and, judging from the ratio of the width of the lines to the distance between the spectra of adjacent orders, the total observable width was about 0.13 Ang.

The absorption of the vapour in the glass bulbs was also examined with the echelon, employing the flame as a source. A distinct increase in the reversal of the  $D_2$  line was observed, when the temperature of the bulb reached  $120^\circ$ . The diameter of the bulb was only 5 cm., and it is probable that with an absorption-tube one metre in length the absorption could be detected at a temperature not very much above the melting-point of the metal.

No attempt was made to photograph the spectrum of the resonance radiation excited by  $D_1$ , as it is quite certain that, if the frequency of  $D_2$  does not give rise to  $D_1$ , the same will hold true for  $D_1$ , as in all cases of resonance spectra the wave-lengths longer than those of the exciting light are much more intense than the shorter ones.

The mechanisms which produce the  $D_1$  lines are not, however, isolated completely, for it has been shown by one of us \* that excitation of the vapour in the region of the channelled spectrum by means of blue-green light causes the appearance of the D lines in the emission spectrum, or at least of a yellow band which coincides with the position of the D lines. This band may, however, correspond to a curious band spectrum which is symmetrical about the D lines which appeared in the spectrum excited by the cathode rays.

Laboratory of M. Bouty,  
La Sorbonne, Paris.

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CIX. *Photometric Investigation of the Superficial Resonance of Sodium Vapour.* By L. DUNOYER and R. W. WOOD †.

[Plate XVII. figs. 8 & 9.]

THE vapour of sodium, relatively cold, is capable of re-emitting the D line radiations, when one concentrates on it light containing these same radiations. This was demonstrated by one of us ‡ in 1905, the image of an oxy-hydrogen sodium flame being formed by a large condenser along the axis of a highly exhausted tube containing a fragment of metallic sodium heated by a small Bunsen flame. At the same time it was shown that the cone of luminosity formed by the exciting rays retreated towards the wall, as the density of the vapour increased until there remained only a thin skin of yellow light, which lined the inner wall of the tube.

The experiment, as carried out at this time, was of short duration, and it did not appear possible to carry on any extensive investigations, with the disposition of the apparatus then employed.

The method of exciting the resonance has, however, recently been greatly improved by one of us § by using small glass bulbs, the walls of which are very carefully freed from occluded gases by prolonged heating, pure sodium being introduced into them by distillation. A further improvement consists in the employment of a Meker burner fed by

\* Wood, *Phil. Mag.* x. p. 408 (1905).

† Communicated by the Authors.

‡ Wood, *Phil. Mag.* x. p. 513 (1905).

§ Dunoyer, *Journal de Physique*, iv. p. 17 (1914).

the spray of a very dilute solution of sodium chloride as a source of light, and forming an image of it on the wall of the bulb by an aplanatic condenser of very large aperture. The sharpness of this image permits of a study of the phenomenon of *secondary resonance* discovered by one of us in the case of the vapour of mercury and described recently\*.

The surface of the bulb, illuminated in the manner described, becomes the source of a resonance radiation of remarkable brilliancy, of a thickness too small to be observed; as the duration of the phenomenon is ten or fifteen hours, it may be investigated photometrically or spectroscopically without difficulty. The preliminary study showed that the intensity of the resonance is much greater if a flame relatively poor in sodium is employed, than with a powerful flame such as is obtained if a fragment of salt is placed on the grill of a Meker burner. If the bulb is heated by a large flame coloured only by the sodium in the air of the room (previously charged by the operation of an intense soda-flame for a few minutes), one observes the yellow glow of the superficial resonance excited by the light emitted by the flame used for the heating of the bulb. The flame must be waved about rapidly over the surface of the bulb, in order to secure a fairly uniform temperature. The phenomenon is less marked if an intense sodium flame is employed.

These experiments show that the greater part of the D light of the flame is inoperative in exciting the resonance. Moreover, the intensity of the source appears scarcely diminished if it is viewed through the bulb in which resonance is taking place. In other words, it is only the central cores of the D lines which are effective in exciting the resonance. The same phenomenon was observed in the study of the resonance of mercury vapour already alluded to, the luminosity (ultra-violet) excited by the 2536 line being enormously greater when the exciting mercury arc was first started, than after it had been in operation for a few seconds.

In the present communication we shall discuss :—

- (1) The photometric study of the diffusing power of the highly attenuated vapour for monochromatic light, as compared with that of a white matt surface of magnesium oxide.
- (2) The conditions under which all of the light removed from the exciting beam is re-emitted, giving us a diffuse reflecting power equal to that of the magnesium oxide.

\* Wood, Phil. Mag. May 1912.

- (3) The probable width of the spectrum lines emitted by the resonating vapour.

*Apparatus employed.*

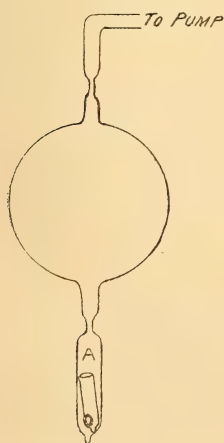
The source of light for exciting the resonance was a Meker burner surrounded by an iron chimney perforated with a rectangular aperture. The burner was fed at the base with a spray formed by an atomizer operated by compressed air. A nearly saturated solution (30 grs. to the litre) of NaCl was diluted to  $\frac{1}{32}$ ,  $\frac{1}{64}$ ,  $\frac{1}{128}$ ,  $\frac{1}{256}$ ,  $\frac{1}{512}$ ,  $\frac{1}{1024}$  and  $\frac{1}{2048}$ , and these solutions introduced in turn into the bulb of the atomizer, previously well rinsed out with a solution of the concentration employed.

An image of the window in the iron chimney was formed on the wall of the bulb by an aplanatic condenser of the type described recently by one of us\*, having a diameter of 11 centimetres and a focus of 12 cm. for parallel light. For divergent light, as in the present case, the source and image are each 25 cm. from the lens.

As the sodium bulbs used in these experiments are very easily made, and are extremely convenient for illustrating

resonance radiation, it may be well to devote a few words to the manner of preparing them. The bulbs are 5 cm. in diameter, drawn down to 1 mm. capillaries as shown in fig. 1. The sodium must first be heated to fusion in a small test-tube and poured out on a cool surface. A piece about  $2 \times 2 \times 2$  mm. is introduced into a small piece of very thin-walled glass tubing, closed at one end, and this capsule placed in the lower tube A, which serves as the distillation chamber. The lower end of A is now closed in the flame of a blast-lamp, and the tube sealed to the mercury pump. After exhausting to a pressure of .001 mm. the bulb is heated for four or five minutes with a large Bunsen flame, the pump working all

Fig. 1.



the while. It should be heated as hot as possible without collapsing. After the bulb has cooled off, the flame is carefully applied to the chamber A, and the sodium distilled into

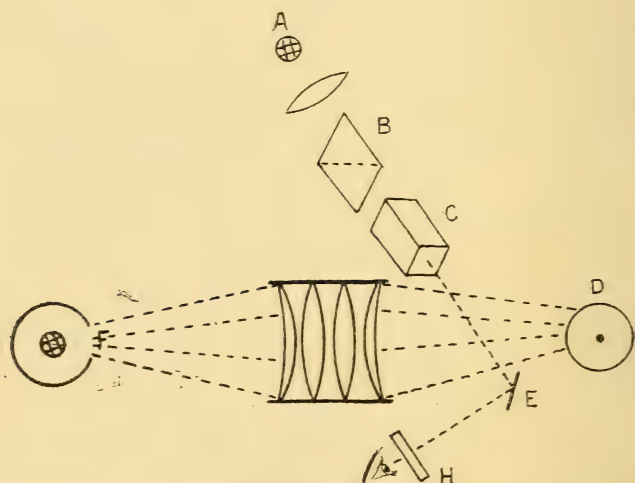
\* Dunoyer, *Journal de Physique*, iii. p. 468 (1913).



the bulb. The lower capillary is then sealed, and finally the upper. The pump should be working vigorously all the while, as the brilliancy of the resonance depends upon having the highest possible vacuum. In our experiments we heated the bulb for twenty minutes, to make sure of getting rid of all of the gases, and the sodium was previously heated *in vacuo*, but these extreme precautions are not necessary in the preparation of bulbs for lecture purposes.

The bulb was supported by a wire in a column of hot air rising from a large tube of fireclay with a large Meker burner at the bottom, by means of which a fairly uniform temperature up to  $400^{\circ}$  could be obtained. For lecture purposes it is sufficient to heat the bulb by waving a large Bunsen flame over its entire surface. The arrangement of our apparatus is shown in fig. 2. As a standard source of

Fig. 2.



comparison we used a sodium flame A behind a piece of ground glass mounted behind a pair of large Nicol prisms B and C. The sodium bulb D was first coated with magnesium oxide, by holding it above a piece of burning Mg ribbon. It was then wiped clean, a small square patch of the oxide being left on one side. The image of the window in the iron chimney surrounding the exciting sodium flame F was formed upon the square of magnesia and the adjacent clear glass of the bulb. It was our object to measure the ratio of the intensity of the magnesia and the vapour of sodium under equal illumination. This was done by means of a very

simple photometer which consisted of a thin scale of silvered glass E, with a razor edge, made by silvering a piece of plate glass, polishing it, and then striking the edge with a hammer. This mirror reflected the comparison source A to the eye through a cell H containing a solution of bichromate of potash (to remove the green and blue rays of the Bunsen flame). Behind the sharp edge of the silver mirror the illuminated surfaces of magnesia and sodium vapour could be seen at the same time, and by adjusting the Nicol prism C the edge of the mirror could be made to disappear, first when seen against the magnesia and secondly against the background of resonating vapour. The intensities of the two surfaces are then in the ratio of the squares of the angles through which C is turned from the position of extinction. The temperature to which the bulb was heated by the ascending current of hot air was about  $330^{\circ}$ , measured with a nitrogen mercury thermometer.

The results are given in the following table, the concentrations of the salt solution in the atomizer bulb in the first column, the angles of the Nicol prism C in the next two columns, and the ratio in the fourth.

Solution Concentration.	Angle $\alpha$ of Nicol for Resonance Radiation.	Angle $\alpha'$ of Nicol for Magnesia.	Ratio $\frac{\sin^2 \alpha'}{\sin^2 \alpha}$ I' (Magnesia) I Sodium vapour.
$\frac{1}{2048}$	$3^{\circ}$	$6^{\circ}$	4
$\frac{1}{1024}$	$9^{\circ} \cdot 25$	$19^{\circ}$	4.5
$\frac{1}{512}$	$10^{\circ} \cdot 5$	$22^{\circ} \cdot 5$	4.8
$\frac{1}{256}$	$13^{\circ} \cdot 5$	$36^{\circ} \cdot 4$	6.3
$\frac{1}{128}$	$14^{\circ} \cdot 4$	$45^{\circ}$	9.6
$\frac{1}{64}$	$14^{\circ}$	$67^{\circ}$	15
$\frac{1}{32}$	$12^{\circ} \cdot 6$	$90^{\circ}$	19

We see from this table that even with the most dilute solution the diffuse reflecting power of the magnesia is four

times as great as that of the resonating sodium vapour, for the total yellow light of the flame. This is of course due to the circumstance that the magnesia reflects all of the D light, while the vapour scatters only the light corresponding to the cores of lines, the light of the edges of the lines being transmitted. As the concentration increases the intensity of the resonance radiation increases but slightly after a certain point is reached, since the gain in the intensity of the sodium flame then results chiefly from a widening of the lines.

For the most concentrated solution ( $\frac{1}{32}$ ) the magnesia was 19 times as intense as the vapour. On reducing the air-current until the yellow colour of the flame was barely visible, a ratio of 3 was obtained, the values of the angles being  $2^\circ$  and  $3^\circ.5$ . This result was, however, open to question on account of the faintness of the light.

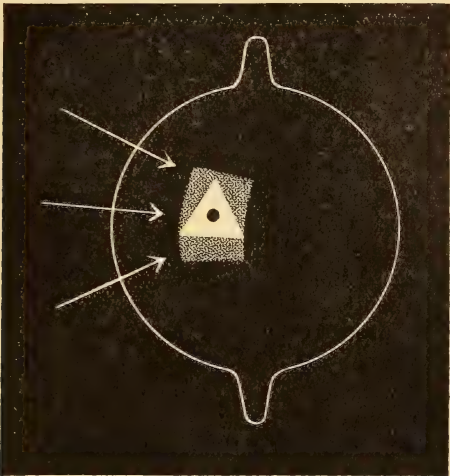
The above results are in accord with those previously obtained by one of us by a different method\*.

If now the molecular resonators absorb none of the light which they abstract from the exciting beam, we ought, if the exciting radiations are made sufficiently homogeneous, to have all of the light diffusely reflected by the vapour; in other words, our ratio ought to sink to unity when the D lines in the source become infinitely narrow. It is impossible to reach this point by diminishing the amount of sodium in the flame, our lowest value for the ratio being four, or perhaps three.

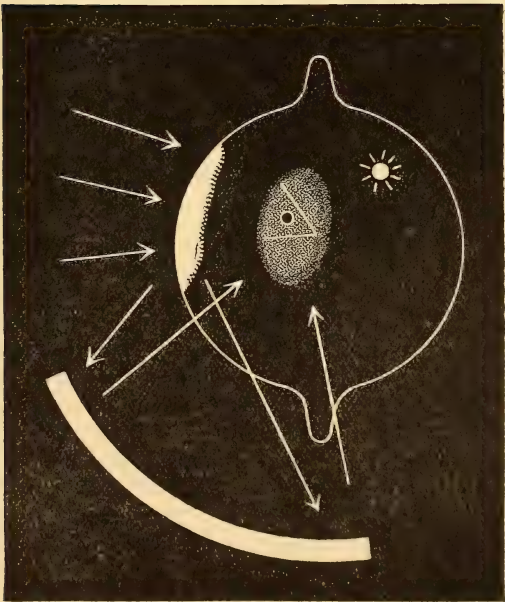
We have, however, investigated the matter by employing the principle of the resonance lamp previously described by one of us, which has been used in the investigations on the resonance of mercury vapour. The experiment was made by utilizing the spot of superficial resonance as a source of light for exciting the vapour at a different point on the surface of the bulb. The arrangement of the apparatus is shown in fig. 3. A small triangular spot of magnesia was formed on the surface of the sodium bulb with a black dot of lamp-black at its centre to indicate its position. The image of the sodium flame was thrown upon this spot, and the magnesia triangle shone brilliantly upon the less intense background of the resonance radiation (fig. 3, *a*). The bulb was now rotated until the triangle of magnesia was in darkness, and an image of the spot of resonance radiation thrown upon it by means of a large concave mirror, formed by

\* L. Dunoyer, *Journal de Physique*, iv. p. 17 (1914).

Fig. 3.



a.



b.



silvering one surface of a double convex lens. Under these conditions the magnesia triangle, and the resonance radiation (which may be termed secondary) which surrounded it had practically the same intensity. In fact it was only with difficulty that the outline of the triangle could be seen, the black dot being surrounded by a uniform glow of light of oval outline (fig. 3, *b*).

Photographs taken of the phenomena are reproduced on Pl. XVII. figs. 8 and 9, the latter showing the disappearance of the magnesia triangle, when the area is illuminated by resonance light reflected from the mirror. The brilliantly illuminated area to the left is the primary resonance excited by the rays from the flame. A narrow dark line partially outlines the triangle; this is due to the shadow thrown upon the resonating vapour by the edges of the layer of magnesia.

The complete disappearance of the triangle was observed only when the flame for exciting the primary resonance was very poor in sodium. We thus have a ratio equal to unity when the exciting rays are sufficiently homogeneous, and can safely say that no true absorption exists in the case of sodium vapour at very low density and in a high vacuum, though the spectroscope would of course show an absorption line. All of the energy abstracted from the primary beam is re-emitted by the molecules, precisely as was found for mercury vapour.

*Probable width of the resonance lines.*

The experiments which we have just described show that the resonance radiation of sodium is excited by the narrow central regions of the D lines.

Let ABC of fig. 4 represent the intensity curve of one of the exciting lines, and the dotted curve DBE the region effective in exciting resonance. The intensity curve of the emitted resonance radiation will be of similar dimensions and may be represented by F. The ratio of the area of the curve ABC to the area of DBE is obviously the ratio found by the photometric measurements, and if we know the form of the curves, and the actual dimensions of ABC (*i. e.* the width of the line in the flame spectrum), we can, from our experimentally found ratio of 4 : 1, determine the width of DBE, the line of the resonance radiation.

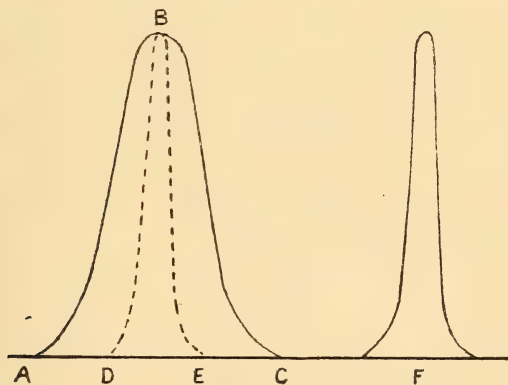
The interferential measurements of Fabry and Buisson have shown that the widths of the D lines emitted by a flame poor in sodium are 0.08 Å.

The law of the partition of energy in spectrum lines furnished by the kinetic theory of gases is

$$y = Ce^{-kx^2}, \quad . . . . . (1)$$

in which  $y$  is the intensity at a distance equal to  $x$  from the centre of the line (at which point the intensity is  $C$ ), and  $k$  gives us the rate at which the intensity falls off as we depart from the centre.

Fig. 4.



The width  $2\epsilon$  of a spectrum line, as defined by Fabry and Buisson, is the distance between two ordinates at distances  $\epsilon$  from the centre, of value equal to  $\frac{C}{2}$ , i. e. an intensity one-half as great as that at the centre of the line.

This gives us

$$\frac{1}{2} = \frac{Ce^{-k\epsilon}}{C} \quad \text{and} \quad e^{-k\epsilon} = \frac{1}{2}, \quad \text{or} \quad \sqrt{k}\epsilon = \sqrt{\log 2}. \quad . . . . . (2)$$

The total intensity of the line being the area comprised between the curve and the axis of abscissæ, we have

$$I = \int_0^{\infty} Ce^{-kx^2} dx = \frac{C\sqrt{\pi}}{\sqrt{k}}. \quad . . . . . (3)$$

If we assume that the portion of the exciting line effective in exciting the resonance is comprised between the ordinates situated at  $-x_1$  and  $+x_1$  (which is of course an approximation since in reality the exciting portion of the line is as shown by the dotted curve of fig. 4), we have, for the

intensity removed from the line by the resonating molecules,

$$I' = \int_{-x_1}^{+x_1} C e^{-kx} dx = \frac{2C}{\sqrt{k}} \int_0^{\sqrt{k} x_1} e^{-u^2} du,$$

or for the ratio

$$\frac{I'}{I} = \frac{2}{\sqrt{\pi}} \int_0^{\sqrt{k} x_1} e^{-u^2} du.$$

Now the value of  $\frac{I'}{I}$  has been determined by the photometric experiments. For the concentration  $\frac{1}{2048}$ , or the flame containing the least amount of sodium  $\frac{I'}{I} = 0.25$ .

From this value and the tables of integrals (Calculus of Probabilities of M. Bachlier) we can calculate the value of the upper limit

$$\sqrt{k} x_1 = 0.0225; \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and by division (equations 2 and 4)

$$\frac{x_1}{\epsilon} = 0.27. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

We may obtain an approximate value of  $x_1$  if we take for  $\epsilon$  the value given for a feeble sodium flame by Fabry and Buisson,

$$\epsilon = 0.04 \text{ \AA}.$$

Inserting this value in equation (5) gives us

$$x_1 = 0.0108 \text{ \AA},$$

or, since  $x_1$  is the half width of the region required, for the width of the region effective in exciting resonance,

$$2x_1 = 0.021 \text{ \AA},$$

the probable width of the resonance lines in contrast to

$$2\epsilon = 0.08 \text{ \AA},$$

the width of the flame lines.

We thus see that by means of sodium vapour at low temperature we can manufacture, so to speak, light much more homogeneous than the incident light, the method being somewhat analogous to that of the Residual Rays of Rubens and Nichols.

It is highly probable that the width of the region removed from the exciting line is identical with the width of the re-emitted resonance radiation. The lines obtained in this

way are thus only one quarter of the width of the lines emitted by the flame and narrower than the iron arc lines.

They are, however, three times as wide as the narrowest known line, the red line of cadmium, for which

$$2\epsilon = \cdot 006 \text{ \AA.}$$

An interferometer study of the resonance radiation is much to be desired, for the above method of deducing the width of the lines is somewhat circuitous.

Laboratory of M. Bouty,  
La Sorbonne, Paris.

## CX. *Proceedings of Learned Societies.*

### GEOLOGICAL SOCIETY.

[Continued from p. 540.]

January 21st, 1914.—Dr. Aubrey Strahan, F.R.S., President,  
in the Chair.

THE following communications were read:—

1. 'Geology of the Country round Huntly (Aberdeenshire).  
By William Robert Watt, M.A., B.Sc., F.G.S.

In this area two distinct series of rocks can be distinguished—a foliated, and a non-foliated series. In the former occur rocks originally sedimentary and others originally igneous. In the non-foliated series, which is wholly of igneous origin, three main intrusions occur:—(1) The earliest and most extensive is a norite with, as modifications due to differentiation, olivine-gabbros, troctolites and 'picrites.'

(2) Into this is intruded the heterogeneous mass known as the Central Intrusion, which consists of three main types with no distinct boundaries:—

(a) At the margin occurs a fine-grained norite with pronounced mineral banding. Nearer the centre of the mass is met (b) a biotite-plagioclase rock; and the centre itself is composed of (c) a garnet-monzonite.

(3) The third large intrusion is the Carvichen Granitite, composed chiefly of quartz, microcline, and biotite.

Each of these masses produces some contact-alteration in the surrounding foliated or non-foliated rocks. Where the Central Intrusion or the Carvichen Granitite is intruded into the earlier norite, a norite containing cordierite is produced. The original norite, by absorption of sediment, produces also along its margin a cordierite-norite. Similar types have been described by Prof. A. Lacroix and Mr. A. N. Winchell.

Both types of cordierite-norite tend to pass into a rock composed essentially of plagioclase, biotite, and garnet; and this change, with the gradual destruction of the hypersthene, can be seen in various stages.



2. 'The Glacial Geology of East Lancashire.' By Albert Jowett, D.Sc., F.G.S.

The area dealt with comprises the western slopes of the Pennines, from Baulsworth Hill to Blackstone Edge, and their westerly offshoot, the Rossendale highland, which separates the basin of the Ribble from that of the Irwell and Mersey.

Three types of drift have been recognized :—

- (1) Local drift, consisting of materials which can be found *in situ* in the neighbourhood, chiefly Coal Measures and Millstone Grit.
- (2) Ribblesdale drift with Carboniferous Limestone, chert, and Silurian grit, as well as local material.
- (3) North-western drift which, in addition to any or all of the above-mentioned constituents, contains igneous rocks from the Lake District and the South-West of Scotland.

The distribution of the drift and the evidence of striated rock-surfaces suggest the invasion of this area by an ice-sheet which reached up to the Pennine watershed, and projected ice-lobes across it through the gaps at Widdop, Gorpel, Cliviger, and Walsden.

A small unglaciated region occurs a few miles south-west of Todmorden.

In the north-eastern portion of the area the general direction of ice-movement was from north to south; in the west it was from north-north-west to south-south-east, but on the south of the Rossendale highland the direction of flow curved round towards the east-north-east, and ultimately, in the neighbourhood of Rochdale, towards the north.

The local drift is believed to have been produced by the overlapping of 200 feet or so of clean ice, which formed the upper portion of the ice-sheet, beyond the limits reached by the ice containing erratics. No evidence of local glaciation has been found.

The limit of the north-western drift rises at the rate of about 4 feet per mile from Blackstone Edge towards the Irish Sea: therefore, when at its maximum, the ice-sheet was probably over 2000 feet above present sea-level in the middle of the Irish Sea in this latitude.

Extensive systems of glacier-lakes and drainage-channels were produced on the retreat of the ice, and for some time the drainage on the west of the Pennines in the Ribble and Irwell basins escaped eastwards into the Yorkshire Calder.

It is probable that the north-western ice arrived in this area later, and disappeared earlier, than the Ribblesdale ice.

Some local fluctuations in the ice-sheet occurred, but there is no evidence for more than one Glacial Period.

February 4th.—Dr. Aubrey Strahan, F.R.S., President, in the Chair.

The following communications were read :—

1. 'The Lithology and Composition of Durham Magnesian Limestones.' By Charles Taylor Trechmann, B.Sc., F.G.S.

The present communication is the result of a somewhat close

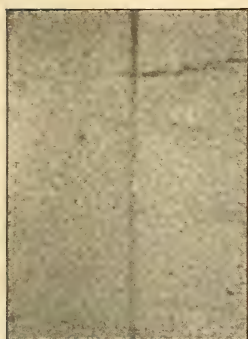


FIG. 1.

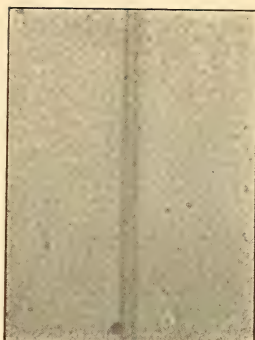


FIG. 2.

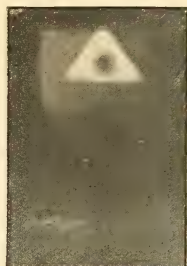


FIG. 8.

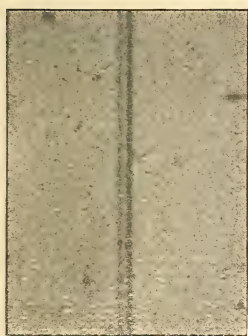


FIG. 3.

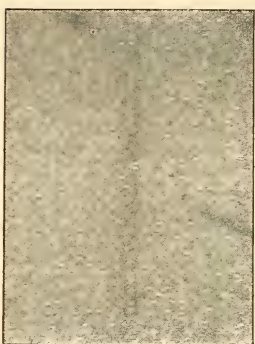


FIG. 4.

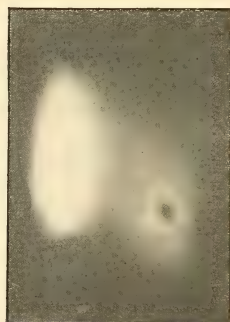


FIG. 9.

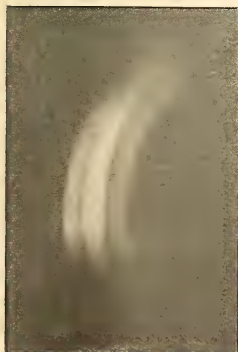


FIG. 5.



FIG. 6.

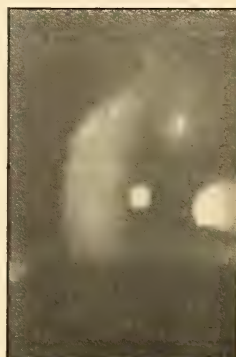


FIG. 7.

70

enquiry into the composition and lithology of the Magnesian Limestones of Durham in all their divisions and conditions of alteration. More than ninety analyses were carried out, of which seventy-eight are herewith presented. Several of the rocks were sliced and stained with Lemberg's solution.

Care was exercised, before a sample was taken, to ascertain the degree of alteration, through segregation or otherwise, which the rock had suffered.

The results show that the formation maintains, generally speaking, a highly dolomitic character, with certain important exceptions. Those portions which show a calcareous composition may be regarded as the result of one of three main causes:—

(1) Original conditions of sedimentation, during which dolomitic deposition or processes of secondary dolomitization were temporarily arrested. Calcareous beds with a brachiopod fauna are extensively developed near the base of the Lower Limestone in the south-western portion of the area.

(2) Escape from secondary dolomitization. Portions of the Shell-Limestone reef, notably at Tunstall Hill, from causes only partly explicable, have escaped conversion into dolomite.

(3) Calcareous segregation, penecontemporaneous with, or subsequent to, deposition.

The paper is intended to be purely a record of observed facts, and no theoretical questions are raised; but internal evidence on several points is brought forward in favour of the view of direct sedimentation of dolomite from the waters of the Permian sea. The view that the bedded dolomites are the result of secondary dolomitization of calcareous organisms is a very improbable one. The question of the secondary dolomitization of the Shell-Limestone reef is discussed.

The dedolomitization of the formation is due to the mechanical washing-away of powdery dolomitic material through the interstices of the rock. The nature of this material was investigated chemically and microscopically. It results from the withdrawal of interstitial calcite, both through former processes of segregation and under existing conditions through the action of percolating water.

No evidence of any leaching-out of magnesium carbonate from the rock was found. Dolomite, even in a fine state of division, is almost insoluble relatively to calcite, but a question certainly arises as to whether such was also the case in earlier periods, in presence of saturated or supersaturated solutions of sulphates.

The nature and distribution of the true cellular rock is discussed, and modes of origin are suggested.

Some general deductions are drawn from evidence of insoluble residues.

Finally, a summary of the general conditions of deposition of the Durham Permian, from the Marl Slate upwards to the Salt Measures, is given, so far as seems legitimately deducible from the available facts.

2. 'On the Occurrence of a Giant Dragon-Fly in the Radstock Coal Measures.' By Herbert Bolton, M.Sc., F.R.S.E., F.G.S., Reader in Palæontology in the University of Bristol.



## INDEX TO VOL. XXVII.

- ACIDS**, on the brush discharge in weak, 801.
- Actinium, on the diffusion of, 591; on the transformations in the active deposit of, 690.
- emanation, on the period of transformation of, 720.
- Adams (Prof. E. P.) on electromagnetic effects related to the Hall effect, 244.
- Æther, on an experiment indicating that matter takes up no room in the, 843.
- Air-pressures, on the, used in playing reed instruments, 271.
- Allen (A. O.) on the slip-curves of an Amsler planimeter, 643.
- Alpha particles, on the collision of, with light atoms, 499; on the passage of, through hydrogen, 824.
- rays, on the recombination of ions made by, 755.
- Amsler planimeter, on the slip-curves of an, 643.
- Andrade (Dr. E. N. da C.) on the wave-length of the soft gamma rays from radium B, 854; on regular surface markings in stretched wires of soft metals, 869.
- Anhyseretic magnetic properties of iron and nickel, on the, 357.
- Anode, on heating effects at the, 189.
- Antimony, on the temperature of sublimation of compounds of, 1.
- Arc, on ionization in the, 277.
- Arsenic, on the temperature of sublimation of compounds of, 2.
- Ashworth (Dr. J. R.) on the anhyseretic magnetic properties of iron and nickel, 357.
- Atoms, on the structure of, 257, 488, 541; on the collision of alpha particles with light, 499; on the forces between, and chemical affinity, 757.
- Balance, on some modifications in an ordinary, 990.
- Baly (Prof. E. C. C.) on light absorption and fluorescence, 632.
- Barton (Prof. E. H.) on ionization and wireless telegraphy, 381.
- Basalt, on the thermal conductivity and specific heat of, 58.
- Bateman (Dr. H.) on the classification of electromagnetic fields, 136.
- Bessel's functions, applications of, to the whispering gallery and allied problems, 100.
- Bismuth, on the temperature of sublimation of compounds of, 10.
- Bohr (Dr. N.) on the effect of electric and magnetic fields on spectral lines, 506.
- Books, new: Researches of the Department of Terrestrial Magnetism, 222; Makower's Practical Measurements in Radioactivity, 222; Annals of the Astrophysical Observatory of the Smithsonian Institution, 396; James Thomson's Collected Papers in Physics and Engineering, 752; U.S. Coast and Geodetic Survey, 752.
- Bragg (Prof. W. H.) on the intensity of the reflexion of X rays by crystals, 881.
- Broek (A. van den) on nuclear electrons, 455.
- Brush discharge, on the electric, in weak acids and solutions, 801.
- Burton (Dr. C. V.) on an experiment indicating that matter takes up no room in the æther, 843.
- Calcium chloride solutions, on the viscosity of, 95.
- Callendar (Prof. H. L.) on the thermodynamics of radiation, 870.
- Campbell (Dr. N.) on delta rays from gases, 83.

- Canonical relations in general dynamics, on, 22.
- Carbon, on the ionization in compounds of, by homogeneous X radiation, 177.
- Cathode disintegration in a vacuum-tube, on, 415.
- Chadwick (J.) on the gamma rays of polonium, radium, and actinium, 112.
- Chemical affinity, on the forces between atoms and, 757.
- Child (C. D.) on ionization in the unstriated discharge and in the arc, 277.
- Chrome steels, on the magnetic properties of, 830.
- Colloids, on the action of, on radioactive products in solution, 618.
- Crystals, on the intensity of reflexion of X rays by, 881.
- Darwin (C. G.) on the theory of X-ray reflexion, 315, 675; on the collision of alpha particles with light atoms, 499.
- Deeley (R. M.) on the Hintereis glacier, 153.
- Delta rays from gases, on, 83.
- Diamond, on the intensity of reflexion of X rays by, 893.
- Differential equations, on the integration of a class of linear, of the second order, 608; on the sum of an infinite series as the solution of, 659; on the integration of, applicable to plane progressive waves, 669.
- Douglas (J. A.) on the geological structure of the S. American Andes, 223.
- Dunoyer (L.) on the separate excitation of the centres of emission of the D lines of sodium, 1018; on a photometric investigation of the superficial resonance of sodium vapour, 1025.
- Dynamics, on canonical relations in general, 22.
- Edmunds (P. J.) on the discharge of electricity from cylinders and points, 789.
- Electrical brush discharge in weak acids and solutions, on the, 801.
- conductivity, on the expression for the, of metals as deduced from the electron theory, 441.
- Electrical discharge, on ionization in the unstriated, 277.
- fields, on the effect of, on spectral lines, 506; on the disintegration of ion clusters in gases under the influence of, 917.
- oscillations, on the effect of ionization of air on, 213; on the theory of, in coupled circuits, 565.
- resistance, on the, of nickel in magnetic fields, 649; on the effect of a magnetic field on metallic, 731.
- waves, on the effect on the propagation of, of the solar eclipse, 753.
- Electricity, notes on, 428; on the discharge of, from cylinders and points, 789.
- Electrification, on the, at liquid-gas surfaces, 297.
- Electrodynamics, on the equations of, and the principle of relativity, 43.
- Electromagnetic effects related to the Hall effect, on some, 244.
- fields, on the classification of, 136.
- Electron atmosphere of metals, on the, 457.
- theory, on the expression for the electrical conductivity of metals as deduced from the, 441.
- Electrons, on the interaction between radiation and free, 14; on nuclear, 455; on the, liberated in ionization, 755.
- Elements, on the high-frequency spectra of the, 541, 703.
- Englund (C. R.) on the electron atmosphere of metals, 457.
- Eve (Prof. A. S.) on the number of ions produced by the gamma radiation from radium, 394.
- Fenninger (W. N.) on the Hall effect in liquid and solid mercury, 109.
- Florance (D. C. H.) on secondary gamma radiation, 225.
- Fluidity, on the influence of volume change on, 662.
- Fluorescence, on the, of iodine vapour, 531; on light absorption and, 632; on the, of gases excited by ultra-Schumann waves, 899.
- Foaming solutions, on a classification of, 718.

- Foord (C. W. H.) on the air-pressures used in playing reed instruments, 271.
- Gamma rays, on the, of polonium, radium, and radioactinium, 112; on secondary, 225; on the, from uranium products, 252; on the number of ions produced by the, from radium, 394; on the absorption of, 601; on the wave-length of the soft, from radium B, 854.
- Gardiner (C. I.) on the Ordovician and Silurian rocks of the Lough Nafooy area, 538.
- Gases, on delta rays from, 83; on the electrification at the surfaces between liquids and, 297; on interference experiments in highly rarefied, 397; on the distribution of energy in the spectra of, 475; on the discharge of electricity through, 789; on the fluorescence of, excited by ultra-Schumann waves, 899; on the disintegration of ion clusters in, under the influence of an electric field, 917.
- Geological Society, proceedings of the, 223, 538, 1035.
- Gibson (W. H.) on the influence of volume change on the fluidity of mixtures, 662.
- Glacier, on the Hintereis, 153.
- Godlewski (Prof. T.) on the action of colloids on radioactive products in solution, 618.
- Granite, on the thermal conductivity and specific heat of, 58.
- Gray (Prof. A.) on canonical relations in general dynamics, 22; notes on electricity and magnetism, 428.
- Hall effect, on the, in liquid and solid mercury, 109; on electromagnetic effects related to the, 244.
- Hargreaves (R.) on Wien's law, 616.
- Hassé (H. R.) on the equations of electrodynamics and the principle of relativity, 43.
- Hemsalech (G. A.) on the fluorescence of gases excited by ultra-Schumann waves, 899.
- Hevesy (Dr. G. von) on the diffusion and valency of the radio-elements, 586.
- Hintereis glacier, on the, 153.
- Hodgson (Dr. B.) on heating effects at the anode in vacuum-tubes, 189.
- Howe (Prof. G. W. O.) on the effect of ionization of air on electrical oscillations, 213.
- Hydrogen, on the ionization in compounds of, by X-radiation, 177; on the passage of alpha particles through, 824.
- Hughes (Dr. A. Ll.) on the long-wave limits of the normal photoelectric effect, 473.
- Hughes (H. G.) on cathode disintegration in a vacuum-tube, 415.
- Images, on the formation of, by an opaque disk, 673.
- Induction-coil potentials, on, 565.
- Integration, on the, of a class of linear differential equations of the second order, 608; on the, of the differential equation applicable to a plane progressive wave, 669.
- Interference experiments in a highly rarefied gas, on, 397.
- Interferometers, on crossed spectra obtained by combinations of, 126.
- Iodine vapour, on the fluorescence of, 531; on the magneto-optics of, 1009.
- Ion cluster, on the disintegration of an, in a gas under the influence of an electric field, 917.
- Ionic dissociation, on the hypothesis of, 459.
- Ionization, on the, in compounds of carbon by X-radiation, 177; on the energy required for, by collision, 269; on, in the unstriated discharge and in the arc, 277; on, and wireless telegraphy, 213, 381; on the electrons liberated in, 755; by collision, on the initial stages of, 963.
- Ions, on the number of, produced by gamma radiation from radium, 394; on the recombination of, made by alpha rays, 755.
- Iron, on the anhyseretic magnetic properties of, 357.
- Isotropic media, on the intrinsic optical activity of, 468; on the rotational optical activity in, 994.
- Jeans (J. H.) on the interaction between radiation and free electrons, 14.



- Jenkins (W. A.) on the effect of a magnetic field on metallic resistance, 731.
- Joly (Prof. J.) on the temperature of sublimation, 1.
- Jones (Prof. E. T.) on induction-coil potentials, 565.
- Jones (W. M.) on the electrical resistance of nickel in magnetic fields, 649.
- Jowett (Dr. A.) on the glacial geology of East Lancashire, 1036.
- Kerschbaum (Dr. F. P.) on interference experiments in a highly rarefied gas, 397.
- Kleeman (Dr. R. D.) on the recombination of ions made by alpha rays, 755; on the electrons liberated in ionization, 755; on the disintegration of an ion cluster in a gas under the influence of an electric field, 917.
- Konen (Prof. H.) on the distribution of energy in the spectra of gases, 475.
- Lander (C. H.) on the application of graphical methods to the solution of problems on struts and tie-rods, 203.
- Langmuir (Dr. I.) on the heat of formation of hydrogen from hydrogen atoms, 188.
- Lead chloride, on the diffusion constants of, 587.
- Le Bas (G.) on the theory of molecular volumes, 344, 740, 976.
- Light absorption and fluorescence, on, 632.
- Liquid-gas surfaces, on the electrification at, 297.
- Liquids, on rotatory polarization in, 91; on the influence of volume change on the fluidity of mixtures of, 662.
- Livens (G. H.) on the intrinsic optical activity of isotropic media, 468; on the rotational optical activity in isotropic media, 994.
- McTaggart (H. A.) on the electrification at liquid-gas surfaces, 297.
- Magnetic field, on the effect of  $\alpha$ , on spectral lines, 506; on the resistance of nickel in  $\alpha$ , 649; on the effect of  $\alpha$ , on metallic resistance, 731.
- properties, on the anhysteretic, of iron and nickel, 357; on the, of chrome steels at ordinary and low temperatures, 830.
- Magnetism, notes on, 428.
- Magnets, on permanent, 428.
- Malam (J. E.) on the electrical resistance of nickel in magnetic fields, 649.
- Marsden (E.) on the transformations in the active deposit of actinium, 690; on the passage of alpha particles through hydrogen, 824.
- Mercury, on the Hall effect in liquid and solid, 109; on regular surface markings in stretched wires of, 869.
- lines, on an anomalous Zeeman effect in satellites of, 333.
- Metallic resistance, on the effect of a magnetic field on, 731.
- Metals, on the expression for the electrical conductivity of, 441; on the electron atmosphere of, 457; on regular surface markings in stretched wires of soft, 869.
- Michelson-Morley experiment, on the physical interpretation of the, 150.
- Mixtures, on the thermodynamical theory of ternary, 942.
- Moir (Miss M. B.) on the magnetic properties of chrome steels at ordinary and low temperatures, 830.
- Molecular volumes, on the theory of, 344, 740, 976.
- Molecule, on the energy required to ionize  $\alpha$ , by collision, 269.
- Monochromatic illumination, on the separation of close spectrum lines for, 524.
- Moore (H.) on the ionization in compounds of carbon by X-radiation, 177.
- Moseley (H. G. J.) on the high-frequency spectra of the elements, 703.
- Nagaoka (Prof. H.) on crossed spectra obtained by combinations of different interferometers, 126; on an anomalous Zeeman effect in satellites of mercury lines, 333.
- Nicholas (T. C.) on the geology of the St. Tudwal's peninsula, 539.
- Nicholson (Prof. J. W.) on the high-frequency spectra of the elements, and the structure of the atom, 541.
- Nickel, on the anhysteretic magnetic



- properties of, 357; on the electrical resistance of, in magnetic fields, 649.
- Oba (S.) on the absorption of gamma rays, 601.
- Optical activity of isotropic media, on the intrinsic, 468; on the rotational, in isotropic media, 994.
- Paris (E. T.) on rotatory polarization in liquids, 91.
- Parr (P. H.) on the Hintereis glacier, 153.
- Peddle (Prof. W.) on the structure of the atom, 257.
- Perkins (Dr. P. B.) on the periods of transformation of thorium and actinium emanation, 720; on the transformations in the active deposit of actinium, 690.
- Photoelectric and photochemical action, on the theory of, 476.
- effect, on the long-wave limits of the normal, 473.
- Planimeter, on the slip-curves of an Amsler, 643.
- Pocock (R. J.) on the action of a disturbing force in the restricted problem of three bodies, 147.
- Polarization, on rotatory, in liquids, 91.
- Polonium, on the gamma rays of, 112.
- Poole (H. H.) on the thermal conductivity and specific heat of granite and basalt, 58; on the activity of freshly-formed radium emanation, 714.
- Porter (Prof. A. W.) on rotatory polarization in liquids, 91; on the formation of images by means of an opaque disk, 673.
- Poynting (John Henry), 914.
- Radiation, on the interaction between, and free electrons, 14; on the thermodynamics of, 870.
- Radioactinium, on the gamma rays of, 112.
- Radioactive products, on the action of colloids on, in solution, 618.
- Radio-elements, on the diffusion and valency of the, 586.
- Radium, on the gamma rays of, 112; on the number of ions produced by the gamma rays from, 394.
- B, on the wave-length of the soft gamma rays from, 854.
- E, on the diffusion of, 590.
- Radium emanation, on the activity of freshly-formed, 714.
- Rails-and-slider magneto-machine, on the, 428.
- Rayleigh (Lord) on applications of Bessel's functions to the whispering gallery and allied problems, 100; on the momentum of progressive waves, 436.
- Reed instruments, on the air-pressures used in playing, 271.
- Relativity, on the equations of electrodynamics and the principle of, 43.
- Resonance, on range and sharpness of, under sustained forcing, 467.
- Reynolds (Prof. S. H.) on the Ordovician and Silurian rocks of the Lough Nafuoey area, 538.
- Ribaud (G.) on the magneto-optics of sodium vapour, 1009.
- Richardson (H.) on the gamma rays from the uranium products, 252.
- Richardson (Prof. O. W.) on the theory of photoelectric and photochemical action, 476.
- Rocksalt, on the intensity of reflexion of X rays by, 889.
- Röntgen radiation, on the distribution of scattered, 383.
- Rose-Innes (J.) on the physical interpretation of the Michelson-Morley experiment, 150; on the integration of the differential equation applicable to a plane progressive wave, 669.
- Russell (Dr. A. S.) on the gamma rays of polonium, radium, and radioactinium, 112.
- Rutherford (Sir E.) on the structure of the atom, 488; on the wave-length of the soft gamma rays from radium B, 854.
- Salt solutions, on the relationship between the viscosity, density, and temperature of, 288.
- Savidge (H. G.) on the integration of a class of linear differential equations of the second order, 608.
- Schwatt (Prof. I. J.) on the sum of an infinite series as the solution of a linear differential equation, 659.
- Selenium, on the temperature of sublimation of compounds of, 13.
- blocks, on the properties of, 370.

- Shakespear (Dr. G. A.) on some modifications in an ordinary balance, 990.
- Shorter (S. A.) on a classification of foaming solutions, 718; on the thermodynamical theory of ternary mixtures, 942.
- Siegbahn (Dr. M.) on the use of the telephone as an oscillograph, 909.
- Simeon (F.) on the viscosity of calcium chloride solutions, 95.
- Smith (H.) on the spectroscopy of the electric brush discharge in weak acids and solutions, 801.
- Smith (S.) on initial stages of ionization by collision, 963.
- Soddy (F.) on the existence of uranium Y, 215.
- Sodium, on the separate excitation of the centres of emission of the D lines of, 1018.
- flame, on the production of a very intense, 530.
- vapour, photometric investigation of the superficial resonance of, 1025.
- Solutions, on the relationship between the viscosity, density, and temperature of salt, 288; on a classification of foaming, 718; on the electric brush discharge in, 801.
- Speas (W. P.) on a photometric study of the fluorescence of iodine vapour, 531.
- Spectra, on crossed, obtained by combinations of different interferometers, 126; on the distribution of energy in the, of gases, 475; on the high-frequency, of the elements, 541, 703.
- Spectroscopy of the electric brush discharge in weak acids and solutions, on the, 801.
- Spectrum lines, on the effect of electric and magnetic fields on, 506; on the separation of close, for monochromatic illumination, 524.
- Steels, on the magnetic properties of chrome, 830.
- Struts, on the application of graphical methods to the solution of problems on, 203.
- Sublimation, on the temperature of, 1.
- Sulphur, on the temperature of sublimation of compounds of, 6.
- Swann (Dr. W. F. G.) on the expression for the electrical conductivity of metals as deduced from the electron theory, 441.
- Takamine (T.) on crossed spectra obtained by combinations of different interferometers, 126; on an anomalous Zeeman effect in satellites of mercury lines, 333.
- Telephone, on the use of the, as an oscillograph, 909.
- Tellurium, on the temperature of sublimation of compounds of, 8.
- Thermal conductivity of granite and basalt, on the, 58.
- Thermodynamics of radiation, on the, 870; of ternary mixtures, on the, 942.
- Thomson (Sir J. J.) on the forces between atoms and chemical affinity, 757.
- Thorium B, on the diffusion of, 587.
- emanation, on the periods of transformation of, 720.
- Three bodies, on the action of a disturbing force in the restricted problem of, 147.
- Tie-rods, on the application of graphical methods to the solution of problems on, 203.
- Townsend (Prof. J. S.) on the energy required to ionize a molecule by collision, 269; on the discharge of electricity from cylinders and points, 786.
- Trechmann (C. T.) on the lithology and composition of Durham magnesian limestones, 1036.
- Tyndall (Dr. A. M.) on cathode disintegration in a vacuum-tube, 415.
- Unstriated discharge, on ionization in the, 277.
- Uranium products, on the gamma rays from the, 252.
- Y, on the existence of, 215.
- Vacuum-tubes, on heating effects at the anode in, 189; on cathode disintegration in, 415.
- Viscosity, density, and temperature of salt solutions, on a relationship between the, 288.
- Waetzmann (Prof. E.) on range and sharpness of resonance under sustained forcing, 467.

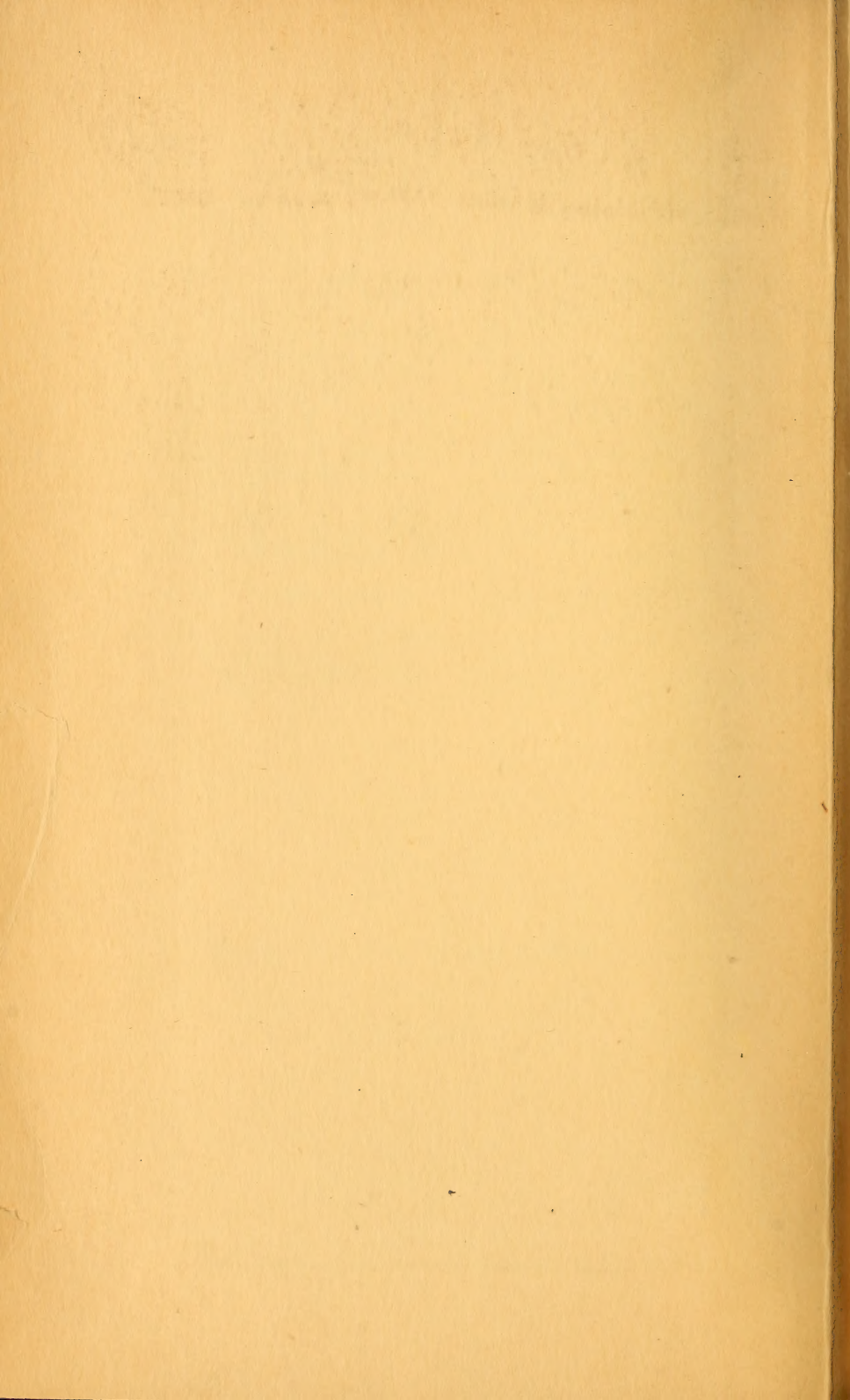
- Walker (W. J.) on the relationship between the viscosity, density, and temperature of salt solutions, 288.
- Watt (W. R.) on the geology of the country round Huntly, 1035.
- Wave-lengths, on the application of crossed spectra to the measurement of differences in, 126.
- Waves, on deep-water, 385; on the momentum of progressive, 436; on the differential equation applicable to plane progressive, 669.
- White (G. W.) on the properties of selenium blocks, 370.
- Whispering gallery, on applications of Bessel's functions to the problem of the, 100.
- Wien's law, on, 616.
- Wilson (Prof. H. A.) on the distribution of scattered Rontgen radiation, 383.
- Wilton (J. R.) on deep-water waves, 385.
- Wireless telegraphy, on ionization of air and long-distance, 213, 381; on the forthcoming eclipse of the sun and, 753.
- Wires, on regular surface markings in stretched, of soft metals, 869.
- Wood (Prof. R. W.) on the separation of close spectrum lines for monochromatic illumination, 524; on the production of a very intense sodium flame, 530; on a photometric study of the fluorescence of iodine vapour, 531; on the fluorescence of gases excited by ultra-Schumann waves, 899; on the magneto-optics of iodine vapour, 1009; on the separate excitation of the centres of emission of the D lines of sodium, 1018; on a photometric investigation of the superficial resonance of sodium vapour, 1025.
- Worley (Prof. F. P.) on the decline of the hypothesis of ionic dissociation, 459.
- X rays, on the ionization in compounds of carbon, hydrogen, and oxygen by homogeneous, 177; on the theory of reflexion of, 315, 675; on the intensity of reflexion of, by crystals, 881.
- Zeeman effect, on an anomalous, in satellites of mercury lines, 333.

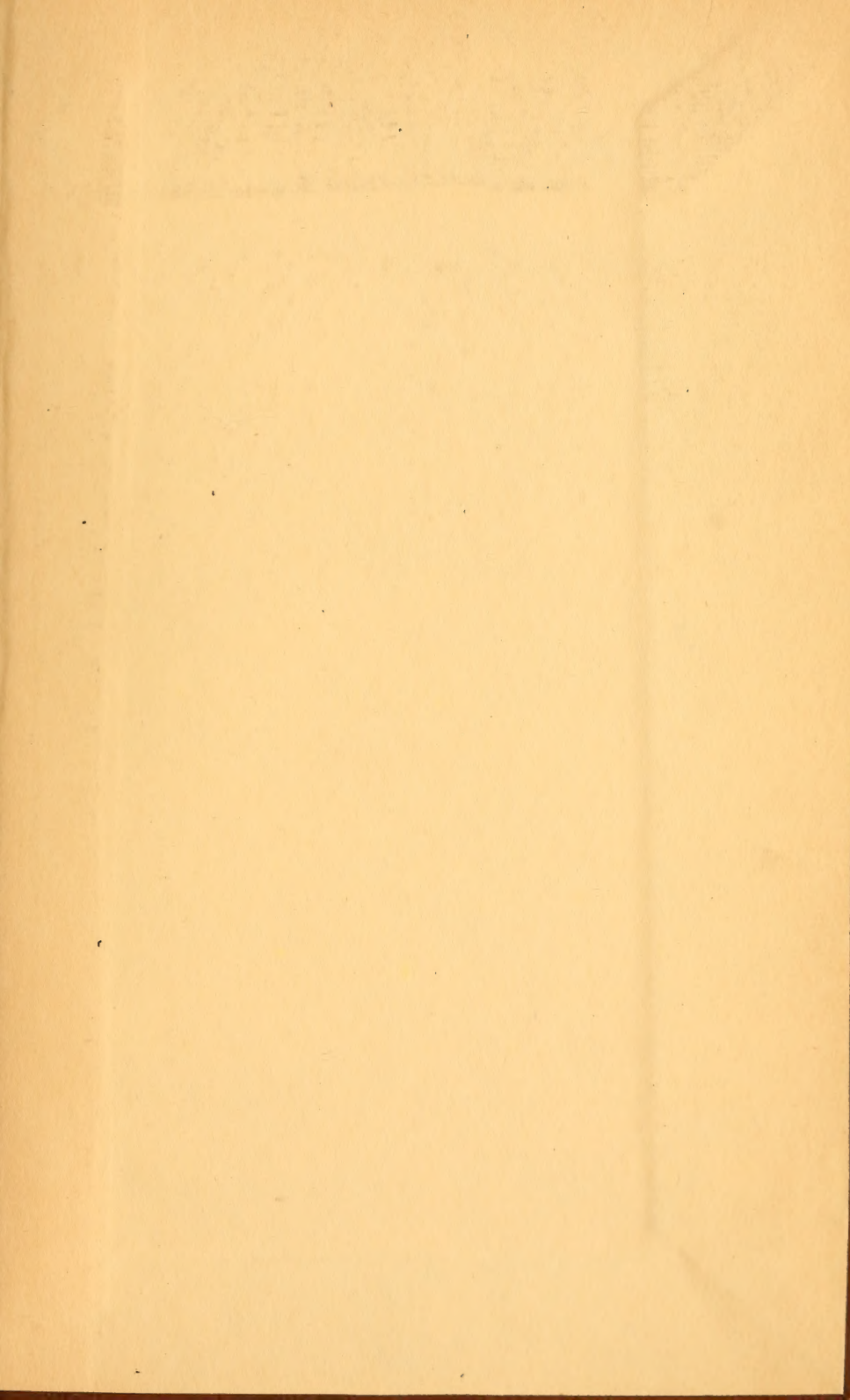
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